

# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XIII

NUMBER 3



*July, 1940*

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1500 Greenmunt Avenue,  
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Vol. XIII

July, 1940

No. 3

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Funk, C. A. 1 Granite St. Brockville, Ontario, Canada	(A)	Goetz, Alvin C. The Eagle-Picher Sales Co. Pigment Division Temple Bar Building Cincinnati, Ohio	(M)
Funk, R. W. 277 Brown St. Akron, Ohio	(M)	Goodman, Leo A. 2301 King's Highway Brooklyn, N. Y.	(M)
Gaffen, J. D. 3900 Dolfield Ave. Baltimore, Maryland	(M)	Gordon, Chester S. 470 Morris Ave. Boonton, New Jersey	(A)
Gage, Roscoe M. 128 Western Ave. Mansfield, Ohio	(M)		

Gorsuch, E. H. Corduroy Tire Co. Grand Rapids, Michigan	(A)	Hall, C. P. C. P. Hall Co. First Central Tower Akron, Ohio	(M)
Gosieniecki, Alfred 403 Kling St. Akron, Ohio	(A)	Hamister, W. P. 1790 Broadway New York, N. Y.	(M)
Gourley, George F. 1230 Sixth Ave. New York, N. Y.	(M)	Hammond, F. W. United Shoe Machinery Corp. Balch St. Beverly, Mass.	(A)
de Graaff, Ir N. V. Philips Gloeilampen- fabrieken Afdeeling Ondervijis en Volkson- twikkeling Bibliotheek-Centrale Kastanjelaan 1 Eindhoven, Holland	(A)	Hand, George F. Box 325 Rouseville, Penn.	(A)
Gray, A. N. Joppa, Maryland	(M)	Hand, J. F. 540 Barwell St. Akron, Ohio	(M)
Gray, Harold 537 Vinita Ave. Akron, Ohio	(M)	Hanley, Albert J. Respro, Inc. Wellington Ave. Providence, Auburn, Rhode Island	(M)
Greene, Leonard Research Dept. Rubber and Asbestos Corp. 26-36 Cornelison Ave. Jersey City, New Jersey	(A)	Hanna, E. L. Davol Rubber Co. Providence, Rhode Island	(M)
Greenup, H. W. 404 Valentine St. Fall River, Mass.	(M)	Hardman, H. V. 47 Riverdale Ave. Belleville, New Jersey	(A)
Grove, John M. 151 W. Pomfret St. Carlisle, Penn.	(M)	Harkins, H. H. U. S. Rubber Co. Providence Plant Providence, Rhode Island	(M)
Guest, Arthur E. Research Dept. Wm. Wrigley Jr. Co. 410 No. Michigan Boulevard Chicago, Illinois	(M)	Harnly, J. W. Griess-Pfleger Tanning Co. Waukegan, Illinois	(M)
Gurney, H. P. Suite 1, 75 Longwood Ave. Brookline, Mass.	(M)	Harrassowitz, Otto Braus-Riggenbach Basle, Switzerland	(A)
Gurnham, C. Fred Chemical Engineering Dept. Pratt Institute Brooklyn, N. Y.	(M)	Harrington, R. A. 277 Storer Ave. Akron, Ohio	(A)
Haas, J. L. Hodgman Rubber Co. Framingham Center, Mass.	(M)	Hart, C. Sheldon 809 East Kingsley St. Ann Arbor, Michigan	(M)
Haberstroh, Robert H. Development, Engineering and Research Dept. American Steel & Wire Co. Cable Works Worcester, Mass.	(M)	Hartman, R. O. 84 Casterton Ave. Akron, Ohio	(A)
Hahn, Stuart H. Box 174 Fairlawn, Ohio	(A)	Hashiguchi, M. No. 18 Hiwaka-Cho Nakano-ku Tokyo, Japan	(A)
Hale, Andrew 2710 First Central Tower Akron, Ohio	(A)	Haslam, G. S. New Jersey Zinc Co. Palmerton, Penn.	(M)
		Hata, Seiichi Honmachi, Tamashima-Cho Okayama-Ken, Japan	(A)



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| Hauser, E. A.<br>16 Fayerweather St.<br>Cambridge, Mass.   | (M) | Hinshaw, G. K.<br>Goodyear Tire & Rubber Co.<br>Akron, Ohio   | (M) |
| Hauser, W. J. R.<br>78 Goodyear Ave.<br>Melrose, Mass.   | (A) | Hirakawa, K.<br>837 Carroll St.<br>Akron, Ohio  | (A) |
| Havenhill, Robert S.<br>1286 Corporation St.<br>Beaver, Penn.                                    | (M) | Hoesly, J. J.<br>Goodyear Tire & Rubber Co.<br>Interplant Relations Dept.<br>Akron, Ohio                                | (M) |
| Hayden, O. M.<br>1018 Overbrook Road, R. D. 1<br>Wilmington, Delaware                            | (M) | Hoffman, H. A.<br>1799 W. Market St.<br>Akron, Ohio   | (M) |
| Haynes, Charles R.<br>405 E. 54th St.<br>New York, N. Y.   | (M) | Holbrook, Frederick L.<br>284 Church St.<br>Naugatuck, Conn.  | (M) |
| Hayworth, Russell A.<br>32 Symon St.<br>Mimico, Ontario<br>Canada                                | (A) | Holmberg, A. W.<br>33 Sweeney St.<br>Naugatuck, Conn.   | (M) |
| Healy, L. J. D.<br>2821 So. Superior St.<br>Milwaukee, Wisconsin                                 | (M) | Holt, W. L.<br>7313 Blair Road, N. W.<br>Takoma Park (Washington), D. C.  | (A) |
| Heggie, Robert<br>Patterson, Simons Co.<br>Singapore<br>Federated Malay States                   | (A) | Homes, Fletcher B.<br>E. I. du Pont de Nemours & Co.<br>Wilmington, Delaware  | (M) |
| Henkel, Paul H.<br>944 West 10th St.<br>Erie, Penn.  | (M) | Hoogstoel, L. E.<br>Behr-Manning Corp.<br>Troy, N. Y.   | (M) |
| Herring, Chas. E. Jr.<br>Holtite Mfg. Co., Inc.<br>Warner and Ostend Sts.<br>Baltimore, Maryland | (M) | Hopkins, G. E.<br>United Shoe Machinery Corp.<br>Baleh St.<br>Beverly, Mass.  | (M) |
| Herrmann, David B.<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.       | (M) | Hopkins, G. E.<br>United States Asbestos Division<br>of Raybestos-Manhattan, Inc.<br>Manheim, Penn.                     | (M) |
| Heymann, Karl<br>American Viscose Co.<br>Meadville, Penn.  | (M) | Hopper, Basil<br>(Corporation representative)<br>Union Oil Co. of California<br>P. O. Box 758<br>Wilmington, California | (M) |
| Hickcox, Ralph T.<br>7108 Holmes Ave.<br>Los Angeles, California                                 | (M) | Horn, A. C.<br>A. C. Horn Co.<br>Horn Building<br>Long Island City, N. Y.   | (M) |
| Hiers, G. S.<br>Collins & Aikman Corp.<br>51st St. and Columbia Ave.<br>Philadelphia, Penn.      | (M) | Hosier, Albert E.<br>2017 Grant St.<br>Cuyahoga Falls, Ohio   | (M) |
| Higgins, John W.<br>P. O. Box 161<br>Warren, Rhode Island  | (A) | Howard, Harry W.<br>903 Jervis Ave.<br>Rome, N. Y.  | (M) |
| Higgins, W. W.<br>United Carbon Co.<br>350 Fifth Ave.<br>New York, N. Y.                         | (A) | Howard, Julian C.<br>Kaufman Rubber Co., Ltd.<br>Kitchener, Ontario<br>Canada   | (M) |
| Hill, George R.<br>12 France St.<br>Norwalk, Conn.   | (M) | Howard, M. F.<br>International Smelting & Refining<br>Co.<br>Pigment Division<br>East Chicago, Indiana                  | (A) |

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| Hucks, W. Richard<br>B. F. Goodrich Co.<br>Akron, Ohio                                      | (M) | Jones, D. E.<br>(Corporation representative)<br>American Hard Rubber Co.<br>Butler, New Jersey                   | (M) |
| Hull, C. O.<br>General Electric Co.<br>Appliance and Merchandise Dept.<br>Bridgeport, Conn. | (A) | Jones, Grinnell<br>Division of Chemistry<br>Harvard University<br>12 Oxford St.<br>Cambridge, Mass.              | (M) |
| Hull, Raymond J.<br>597 Glendora Ave.<br>Akron, Ohio  | (M) | Jones, H. C.<br>202 Princeton Ave.<br>Palmerton, Penn.   | (M) |
| Humphrey, B. J.<br>Firestone Tire & Rubber Co.<br>Akron, Ohio                               | (M) | Jones, P. C.<br>825 Work Drive<br>Akron, Ohio  | (M) |
| Hutchinson, R. E.<br>8121 Madison Ave.<br>Southgate, California                             | (A) | Jones, Warren H.<br>General Cable Corp.<br>56 Clyde Ave.<br>Buffalo, N. Y.                                       | (M) |
| d'Ianni, James<br>893 Columbia Ave.<br>Akron, Ohio  | (M) | Jordan, H. F.<br>U. S. Rubber Co.<br>Market and South Sts.<br>Passaic, New Jersey                                | (M) |
| India Rubber World<br>420 Lexington Ave.<br>New York, N. Y.                                 | (A) | Juve, Robert D.<br>124 Clemmer Ave.<br>Akron, Ohio   | (M) |
| Ingmanson, John H.<br>183 Forbes St.<br>Rahway, New Jersey                                  | (M) | Juve, Walter<br>124 Clemmer Ave.<br>Akron, Ohio  | (M) |
| Ishiguro, Katsumi<br>Tokyo E. C. Kogyo<br>437 Ikezirimachi Setagayaku<br>near Tokyo, Japan  | (A) | Kambara, Shu<br>Tokyo University of Engineering<br>Applied Chemistry Dept.<br>Ohkayama, Meguroku<br>Tokyo, Japan | (A) |
| Jackson, W.<br>Georgia Kaolin Co.<br>230 Park Ave.<br>New York, N. Y.                       | (M) | Karch, Herbert S.<br>R. F. D. 2<br>Cuyahoga Falls, Ohio  | (M) |
| Jansen, J. Eden<br>Research Laboratory<br>B. F. Goodrich Co.<br>Akron, Ohio                 | (M) | Katz, Morris<br>Division of Chemistry<br>National Research Council<br>Ottawa, Canada                             | (M) |
| Jecusco, F. P.<br>Apt. 705, Sheraton Hotel<br>Providence, Rhode Island                      | (M) | Keith, W. P.<br>Hygienic Dental Rubber Co.<br>31 W. Market St.<br>Akron, Ohio                                    | (A) |
| Jeffrey, G. A.<br>Chemistry Dept.<br>The University<br>Edgbaston, Birmingham, 15<br>England | (A) | Keller, A. M.<br>319 Carson Road<br>Ferguson, Missouri   | (M) |
| Jetel, Josef<br>Nederlandsche Schoenen en<br>Lederfabrieken<br>Bata, Best, Nederland        | (A) | Kelley, Herbert W.<br>200 Boston Ave.<br>Medford, Mass.  | (M) |
| Johnson, B. L.<br>766 Glendora Ave.<br>Akron, Ohio  | (M) | Kelly, Arthur<br>B. F. Goodrich Co.<br>Clarksville, Tenn.  | (M) |
| Johnson, D. W.<br>Cia-Hulera "Euzkadi" S. A.<br>Apartado 130 bis.<br>Mexico, D. F.          | (M) | Kelsey, W. F.<br>Easthampton Rubber Thread Co.<br>Easthampton, Mass.   | (M) |
| Johnson, Robert H.<br>33 Winfield St.<br>East Norwalk, Conn.                                | (M) |  |     |

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| Keltie, George R.<br>American Wringer Co., Inc.<br>Woonsocket, Rhode Island                      | (A) | Kuykendall, S. B.<br>Research Laboratories<br>Firestone Tire & Rubber Co.<br>Akron, Ohio                  | (M) |
| Kemp, A. R.<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.              | (M) | Laatsch, M. H., Jr.<br>Goodyear Tire & Rubber Co.<br>Akron, Ohio  | (M) |
| Kempel, A. B., Jr.<br>(Corporation representative)<br>Rex-Hide, Inc.<br>East Brady, Penn.        | (A) | Laszlo, Popper<br>P/A Magyar Ruggyantaarugyar<br>R. T.<br>Postafio 206<br>Budapest, 4, Hungary            | (A) |
| Kennedy, Carl D.<br>215 Main St.<br>Ridgefield Park, New Jersey                                  | (M) | Laughlin, E. E.<br>Pharis Tire & Rubber Co.<br>Newark, Ohio   | (M) |
| Kern, Ervin S.<br>207 East Road<br>Glen Ellyn, Illinois  | (M) | Laurence, Albert E.<br>1057 Bloomfield Ave.<br>Akron, Ohio  | (M) |
| King, R. J.<br>King and Lang, Inc.<br>South Norwalk, Conn.                                       | (M) | Leduc, Henri<br>20 Rue Thiboumery<br>Paris XV°, France  | (A) |
| Kirschner, Jacob<br>Dryden Rubber Co.<br>1014 So. Kildare Ave.<br>Chicago, Illinois              | (M) | Lee, Alan Porter<br>136 Liberty St.<br>New York, N. Y.  | (M) |
| Knapp, R. C.<br>1540 Hawthorne<br>Grosse Pointe Woods, Fox Creek<br>Station<br>Detroit, Michigan | (M) | Lefcaditis, G. D.<br>Leoforos Syngrow 26A<br>Athens, Greece   | (A) |
| Knowland, T. M.<br>35 Toby Road<br>Belmont, Mass.  | (M) | Leiter, C. R.<br>51 E. Marquette Rd.<br>Chicago, Illinois   | (M) |
| Koide, T.<br>The Yokohama Rubber Co.<br>Heiancho, Tsurumi<br>Yokohama, Japan                     | (A) | Lenhart, George B.<br>Wilson Rubber Co.<br>Canton, Ohio   | (M) |
| Kovacs, Frank<br>Seiberling Rubber Co.<br>Akron, Ohio  | (M) | Lessig, E. T.<br>B. F. Goodrich Co.<br>Akron, Ohio  | (M) |
| Krantz, W. J.<br>P. O. Box 467<br>East Akron, Ohio   | (M) | Le Tourneau, Robert<br>199 Elwood Ave.<br>Akron, Ohio   | (M) |
| Krismann, Emil H.<br>78 Washington St.<br>Newton, Mass.  | (M) | Lewis, A. R.<br>Residence Park<br>Palmerton, Penn.  | (M) |
| Kroeger, A. P.<br>605 W. Olympic Boulevard<br>Los Angeles, California                            | (A) | Lewis, Ben W.<br>Research Laboratory<br>Wishnick-Tumpeer, Inc.<br>6100 West 51st St.<br>Chicago, Illinois | (M) |
| Kuckro, Gerard W.<br>45-16 44th St.<br>Long Island City, N. Y.                                   | (M) | Lewis, R. R.<br>Vulcan Proofing Co.<br>First Ave. and 57th St.<br>Brooklyn, N. Y.                         | (M) |
| Kundinger, R. A.<br>Dominion Tire Factory<br>Kitchener, Ontario<br>Canada                        | (M) | Liddick, Harold S.<br>12 Plymouth Road<br>Lexington, Mass.  | (A) |
| Kurtz, Stewart S., Jr.<br>Sun Oil Co.<br>Marcus Hook, Penn.                                      | (M) | Lightbown, Irving E.<br>253 W. 5th Ave.<br>Roselle, New Jersey  | (M) |

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| Linscott, R. F.<br>177 E. Grand Boulevard<br>Detroit, Michigan                          | (M) | MacKay, J. W.<br>Rubber Service Dept.<br>Monsanto Chemical Co.<br>Akron, Ohio                             | (M) |
| Lips, Carl H.<br>24 Madeline Parkway<br>Yonkers, N. Y.                                  | (M) | MacKenzie, W. B.<br>Habirshaw Cable & Wire Corp.<br>Yonkers, N. Y.  | (M) |
| Little, Julian R.<br>General Laboratories<br>U. S. Rubber Co.<br>Passaic, New Jersey    | (M) | Madge, N. Gibson<br>Development Dept.<br>U. S. Rubber Co.<br>Market and South Sts.<br>Passaic, New Jersey | (M) |
| Littman, Joseph B.<br>Packard Electric Division<br>General Motors Corp.<br>Warren, Ohio | (M) | Magee, Cornelius<br>39 Hill Crest Terrace<br>Verona, New Jersey   | (A) |
| Long, Richard E.<br>Seiberling Latex Products Co.<br>Akron, Ohio                        | (A) | Maiden, J. P.<br>96 Overwood Drive<br>Akron, Ohio   | (M) |
| Longstreth, Bevis<br>780 No. Clinton Ave.<br>Trenton, New Jersey                        | (A) | Malm, F. S.<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.                       | (M) |
| Longworth, L. L.<br>1499 Beardsley St.<br>Akron, Ohio                                   | (A) | Marcelo, Jose P.<br>Malabon, Rizal<br>Philippines   | (M) |
| Loomis, George P.<br>R. 2<br>Cuyahoga Falls, Ohio                                       | (M) | Marr, R. B.<br>Dominion Rubber Co., Ltd.<br>Box 330<br>Montreal, P. Q., Canada                            | (M) |
| Loughborough, Dwight L.<br>325 Cloverdale Ave.<br>Akron, Ohio                           | (M) | Martin, F. A.<br>The Hoover Co.<br>North Canton, Ohio   | (M) |
| Lowe, O. E.<br>386 Auburn St.<br>Cranston, Rhode Island                                 | (M) | Martin, F. S.<br>625 Public St.<br>Providence, Rhode Island   | (M) |
| Loy, E. A.<br>47 Colden St.<br>Newark, New Jersey                                       | (M) | Martin, S. M.<br>Thiokol Corporation<br>Trenton, New Jersey   | (M) |
| Lukens, A. R.<br>11 Windsor St.<br>Cambridge, Mass.                                     | (M) | Masland, C. H., 2nd<br>P. O. Box 443<br>Carlisle, Penn.   | (M) |
| Lundgren, Carl<br>Sport Products, Inc.<br>John and Findlay Sts.<br>Cincinnati, Ohio     | (A) | Mathes, Roger A.<br>1597 Delia Ave.<br>Akron, Ohio  | (M) |
| Lupke, Paul, Jr.<br>Essex Rubber Co.<br>P. O. Box 501<br>Trenton, New Jersey            | (M) | Matheson, L. A.<br>2411 Manor Drive<br>Midland, Michigan  | (M) |
| Luth, H. J.<br>Brunswick-Balke-Collender Co.<br>Muskegon, Michigan                      | (A) | Mathews, W. C.<br>Research Division<br>New Jersey Zinc Co.<br>Palmerton, Penn.                            | (M) |
| Maassen, G. C.<br>5756 N. Kent Ave.<br>Milwaukee, Wisconsin                             | (M) | Mathey, G. S.<br>Johnson & Johnson<br>New Brunswick, New Jersey   | (M) |
| Mack, Gerry<br>Room 2203<br>245 Fifth Ave.<br>New York, N. Y.                           | (M) | Matsudaira, Mobutaka<br>Asahimachi<br>Kurume, Japan   | (A) |
| Mack, Gordon C.<br>Patent Dept.<br>Goodyear Tire & Rubber Co.<br>Akron, Ohio            | (M) | McCarty, J. E.<br>Kelly-Springfield Tire Co.<br>Cumberland, Maryland                                      | (M) |

McClelland, G. L. Continental Rubber Works Erie, Penn.	(M)	Midgley, Thomas, Jr. Worthington Ohio	(M)
McClure, R. R. Pure Calcium Products Co. Painesville, Ohio	(M)	Miller, George C. 290 Dodge St. Buffalo, N. Y.	(M)
McColm, Eugene M. U. S. Rubber Co. North Bergen Plant North Bergen, New Jersey	(M)	Miller, Kenneth J. Mellon Institute of Industrial Research University of Pittsburgh Pittsburgh, Penn.	(M)
McCutchan, George L. Rome Cable Corp. Rome, N. Y.	(M)	Miller, S. P. Barrett Co. 40 Rector St. New York, N. Y.	(M)
McDermott, Paul 52 Linwood Ave. Buffalo, N. Y.	(M)	Minatoya, S. No. 201, Nishiochiai, 1-Chome Yodobashiku, Tokyo, Japan	(A)
McDonald, John E. Kelly Springfield Tire Co. Cumberland, Maryland	(M)	Miserentino, C. O. 296 W. Delavan Ave. Buffalo, N. Y.	(A)
McDowell, A. V. Goodyear Rubber Co. Middletown, Conn.	(A)	Mooney, M. General Laboratories U. S. Rubber Co. Passaic, New Jersey	(A)
McHugh, Charles P. 17 Eton Place Glen Rock, New Jersey	(M)	Moore, W. A. Armstrong Tire & Rubber Co. Natchez, Mississippi	(M)
McKenzie, James P. Marbon Corporation 1926 W. Tenth St. Gary, Indiana	(M)	Mooshegranz, G. P. Jenkins Brothers 510 Main St. Bridgeport, Conn.	(A)
McMullen, E. W. Box 552 Joplin, Missouri	(M)	Morgan, C. P. (Corporation representative) Vulcanized Rubber Co. Morrisville, Penn.	(M)
McPherson, A. T. 231 Industrial Building Bureau of Standards Washington, D. C.	(M)	Morgan, Willard L. 72 Massasoit Ave. Edgewood, Rhode Island	(M)
McRoberts, D. C. Gates Rubber Co. Denver, Colorado	(M)	Morris, Harold B. Naugatuck Chemical Division U. S. Rubber Co. 560 Atlantic Ave. Boston, Mass.	(M)
Meadors, Victor G. 337 Paulison Ave. Passaic, New Jersey	(M)	Morris, M. P. 68 Kirkland St. Cambridge, Mass.	(M)
Meek, Howard Federal Color Laboratories, Inc. Norwood, Ohio	(A)	Morris, Ross E. 51 Ventura St. Vallejo, California	(M)
Meeus, E. de Goodrich Place de Valny Colombes (Seine), France	(M)	Morrison, J. D. 1386 Kensington Road Grosse Pointe, Michigan	(M)
Merrill, A. B. Box 664, R. D. 4 Akron, Ohio	(M)	Morton, H. A. 475 Dorchester Road Akron, Ohio	(M)
Merrill, G. S. 1303 Beechwood Ave. St. Paul, Minnesota	(M)	Morton, H. Clifford 257 Lincoln Ave. Highland Park New Brunswick, N. J.	(M)
Meyer, Harold S. 1564 Alton Drive Akron, Ohio	(M)		



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| Moses, Kirke L.<br>Premoid Products Co.<br>Box 1591<br>Springfield, Mass.                           | (A) | Noble, Royce J.<br>21 Woodland Road<br>Malden, Mass.  | (M) |
| Mueller, Carl<br>Room 3000<br>521 Fifth Ave.<br>New York, N. Y.                                     | (M) | Noll, E. M.<br>Noll Chemical Co.<br>220 South Inglewood Ave.<br>Inglewood, California       | (M) |
| Mueller, George S.<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.          | (M) | Nordstrom, Yngve H.<br>10 Indian Lake Parkway<br>Worcester, Mass.                           | (M) |
| Mullaly, A. B.<br>415 Buttermere Ave.<br>Interlaken, New Jersey                                     | (M) | Northam, A. J.<br>Parkway and Seville Avenues<br>Villa Monterey<br>Wilmington, Delaware     | (M) |
| Muller, Robert H.<br>65 Compayne Gardens<br>London, N. W. 6, England                                | (M) | Norton, J. H.<br>5238 General Motors Bldg.<br>Detroit, Michigan                             | (M) |
| Murrill, P. I.<br>R. T. Vanderbilt Co.<br>33 Winfield St.<br>East Norwalk, Conn.                    | (M) | Novotny, C. K.<br>Research Division, Dept. 81<br>Firestone Tire & Rubber Co.<br>Akron, Ohio | (M) |
| Nagy, Louis<br>Parker, Stearns & Co.<br>288-300 Sheffield Ave.<br>Brooklyn, N. Y.                   | (A) | Oakleaf, A. W.<br>8100 East Jefferson Ave.<br>Detroit, Michigan                             | (M) |
| Nankodo, S. Kodachi<br>Haruki-Cho, 3-Chome<br>Hongo, Tokyo, Japan                                   | (A) | O'Brien, Raymond J.<br>27 Walnut St.<br>Rutherford, New Jersey                              | (M) |
| Naylor, R. A.<br>Y. M. C. A.<br>Greenwich, Conn.  | (M) | Odell, Horace B.<br>The Odell Company<br>Morton and Acton Sts.<br>Worcester, Mass.          | (A) |
| Neal, Arthur M.<br>433 Geddes St.<br>Wilmington, Delaware   | (M) | Oenslager, George<br>Pasadena Apartments<br>Twin Oaks Road<br>Akron, Ohio                   | (M) |
| Nellen, A. H.<br>(Corporation representative)<br>Lee Rubber & Tire Corp.<br>Conshohocken, Penn.     | (M) | Oldham, E. W.<br>55 Mount View Ave.<br>Akron, Ohio  | (M) |
| Nelson, Wm. G.<br>558 Philip St.<br>Detroit, Michigan   | (M) | Olin, R. R.<br>P. O. Box 372<br>Akron, Ohio   | (M) |
| Nelson, W. L.<br>Mellon Institute of Industrial<br>Research<br>4400 Fifth Ave.<br>Pittsburgh, Penn. | (M) | Omansky, Morris<br>9 Babcock St.<br>Brookline, Mass.  | (M) |
| Nesbit, Jean<br>U. S. Rubber Reclaiming Co.<br>500 Fifth Ave.<br>New York, N. Y.                    | (A) | Outcalt, H. E.<br>St. Joseph Lead Co.<br>250 Park Ave.<br>New York, N. Y.                   | (M) |
| Neville, C. A.<br>U. S. Rubber Co.<br>5725 Telegraph Road<br>Los Angeles, California                | (M) | Page, Harold D.<br>Waugh Equipment Co.<br>420 Lexington Ave.<br>New York, N. Y.             | (A) |
| Niemeyer, H. J.<br>374 East Catawba Ave.<br>Akron, Ohio   | (A) | Pagel, La Vern<br>Pioneer Rubber Co.<br>Willard, Ohio                                       | (M) |
|   |     | Palmer, H. F.<br>539 Moreley Ave.<br>Akron, Ohio  | (M) |

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| Park, C. R.<br>R. D. 2, Box 117<br>Cuyahoga Falls, Ohio                                       | (M) | Poli, Cino<br>Società Italiana Pirelli<br>Segreteria Centrale Pubblicazioni<br>Associazioni<br>Via Fabio Filzi 21<br>Milano (5/6), Italy | (A) |
| Parrish, Wm. D.<br>B. F. Goodrich Co.<br>Akron, Ohio  | (M) | Pollard, T. N.<br>31 Goodrich St.<br>Akron, Ohio   | (A) |
| Partenheimer, J. E.<br>Atlas Supply Co.<br>744 Broad St.<br>Newark, New Jersey                | (M) | Pomey, M. Jacques<br>Usines Renault<br>Billancourt (Seine), France   | (A) |
| Partridge, Edward G.<br>Box 136<br>Stowe, Ohio  | (M) | Pond, A. F.<br>U. S. Rubber Co.<br>5725 Telegraph Road<br>Los Angeles, California  | (M) |
| Patrick, Joseph C.<br>780 No. Clinton Ave.<br>Trenton, New Jersey                             | (M) | Porini, Giovanni<br>Eberhard Faber Co.<br>Newark, New Jersey   | (M) |
| Patterson, Ian D.<br>St. Mary's Mfg. Co.<br>P. O. Box 215<br>St. Mary's, Ohio                 | (M) | Porthouse, C. R.<br>Pyramid Rubber Co.<br>Ravenna, Ohio  | (M) |
| Peakes, Lawson V., Jr.<br>Box 135<br>Canajoharie, N. Y.                                       | (M) | Post, Howard W.<br>3435 Main St.<br>Buffalo, N. Y.   | (M) |
| Peden, Edgar A.<br>14 E. Caskill Ave.<br>Jeannette, Penn.                                     | (M) | Potter, Wendell J.<br>33 Winfield St.<br>East Norwalk, Conn.   | (M) |
| Peterjohn, A. C.<br>4422 W. 143rd St.<br>Cleveland, Ohio                                      | (M) | Pough, F. H.<br>Southern Acid and Sulfur Co.<br>Rialto Building<br>St. Louis, Missouri   | (M) |
| Peters, Henry<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.         | (M) | Poules, Ira<br>2124 Highbridge Road<br>Cuyahoga Falls, Ohio  | (M) |
| Peterson, J. M.<br>Hercules Experiment Station<br>Hercules Powder Co.<br>Wilmington, Delaware | (M) | Powell, Charles S.<br>84-37 Avon Road<br>Jamaica, Long Island, New York  | (M) |
| Peterson, L. C.<br>Fisk Rubber Corp.<br>Chicopee Falls, Mass.                                 | (M) | Prettyman, I. B.<br>641 Sackett St.<br>Cuyahoga Falls, Ohio  | (A) |
| Phillips, F. E.<br>S. S. White Dental Mfg. Co.<br>Prince Bay<br>Staten Island, N. Y.          | (A) | Price, Gladding<br>Cedar Ave.<br>East Greenwich, Rhode Island  | (A) |
| Phillips, H.<br>Wool Industries Research Assn.<br>Torridon, Headingley<br>Leeds, 6, England   | (M) | Prins, J. Allingh<br>Library "Bureau voor den Indus-<br>trieelen Eigendom"<br>'s Gravenhage<br>Netherlands                               | (M) |
| Picard, R. F.<br>Henrite Products Corp.<br>Ironton, Ohio                                      | (M) | Proskauer, Erich S.<br>215 Fourth Ave.<br>New York, N. Y.  | (M) |
| Pinto, Peter P.<br>Palmerton Publishing Co.<br>250 W. 57th St.<br>New York, N. Y.             | (A) | Protheroe, H. P.<br>709 Wellesley Ave.<br>Akron, Ohio  | (M) |
| Plumb, John S.<br>U. S. Rubber Reclaiming Co.<br>724 Babcock St.<br>Buffalo, N. Y.            | (A) | Quasebarth, K. H.<br>117-01 Park Lane South<br>Kew Gardens, N. Y.  | (M) |

Rafter, J. R. Research Laboratories Firestone Tire & Rubber Co. Akron, Ohio	(M)	Rines, J. Flintkote Co. Morristown, New Jersey	(A)
Ramsay, John Gutta-Percha & Rubber Co., Ltd. West Lodge Ave. Toronto, Ontario, Canada	(A)	Rishor, George Canadian General Electric Co. Peterborough, Ontario, Canada	(A)
Randall, Robert L. Midwest Rubber Reclaiming Co. East St. Louis, Illinois	(M)	Roberts, Edward B. 10 Allston St. Newtonville, Mass.	(A)
Rankin, J. J. 149 Taylor Ave. Beaver, Pa.	(M)	Robertson, J. A. North British Rubber Co., Ltd. Castle Mills Edinburgh, Scotland	(M)
Rash, J. W. Cotan Corporation 331-359 Oliver St. Newark, N. J.	(A)	Robinson, J. E. Footwear Department U. S. Rubber Co. Naugatuck, Conn.	(M)
Rausell, A. F. R. T. Vanderbilt Co. 33 Winfield St. East Norwalk, Conn.	(A)	Robinson, J. G. 6 Horderns Park Road Chapel-en-le Frith Stockport, England	(A)
Read, Barclay K. Box 10 Montreal, P. Q., Canada	(A)	Rockoff, Joseph 1563 No. Euclid Ave. Dayton, Ohio	(M)
Reece, W. H. The Leyland and Birmingham Rubber Co., Ltd. Leyland, near Preston, England	(M)	Ross, Bryant C. Palmyra, New Jersey	(A)
Reed, Marion C. 2208 Concord Drive Lakewood, Ohio	(M)	Rowland, George M. 1927 Burroughs Drive Dayton, Ohio	(A)
Reed, R. F. Director University of Cincinnati Cincinnati, Ohio	(M)	Ruben, Gerhard Kungstradgardsgatan 22 Stockholm, Sweden	(M)
Reid, W. Apt. 5 148 Sanders Road Buffalo, N. Y.	(M)	Rubidge, C. R. 515 Highland Ave. Upper Montclair, New Jersey	(M)
Reinbold, E. B. J. M. Huber Corp. Borger, Texas	(M)	Rubiner, Isidore 1840 Grand Concourse New York, N. Y.	(M)
Reinhardt, F. 124-06 116th Ave. Richmond Hill, Long Island, N. Y.	(A)	Ruch, Elden H. Laboratory Firestone Tire & Rubber Co. Memphis, Tenn.	(M)
Rente, A. M. 5248 Helen Ave. Detroit, Michigan	(M)	Rupert, F. E. 31 Goodrich St. Akron, Ohio	(M)
Rhee, Daniel 875 Hope St. Bristol, Rhode Island	(M)	Russell, J. J. General Electric Co. 1 River Road Schenectady, N. Y.	(M)
Rhodes, Louis 1746 E. Market St. Akron, Ohio	(M)	Russell, W. F. P. O. Box 85 Norwalk, Conn.	(M)
Rice, P. E. 38 Walnut St. Naugatuck, Conn.	(M)	Ryan, Albert O. Behr-Manning Corp. Troy, N. Y.	(M)
		Sackett, George A. 615 Roslyn Ave. Akron, Ohio	(M)

Sanderson, Clifford W. Terry Road, R. F. D. Hudson, Ohio	(M)	Sellon, John American Zinc Sales Co. 420 Lexington Ave. New York, N. Y.	(M)
Sato, Shigeo Toyota-Jidosha-Kogyo- Kabushiki-Kaisha Kariya-Kojo, Kariya-Cho, Hekkai-gun Aichi-Ken, Japan	(A)	Semon, Waldo L. R. D. 2, P. O. Box 104 Cuyahoga Falls, Ohio	(M)
Scarrow, J. A. Sterling Rubber Co., Ltd. Guelph, Ontario, Canada	(A)	Shaffer, C. R. Xylos Rubber Co. Akron, Ohio	(A)
Schade, James W. 189 Merriman Road Akron, Ohio	(M)	Shepard, Alvin F. 41 Southwood Drive Kenmore, N. Y.	(M)
Schaefer, Fred C. 301 Sumner St. Akron, Ohio	(M)	Shepard, N. A. 93 Old Church Road Greenwich, Conn.	(M)
Schar, R. S. Box 428 East Brady, Penn.	(M)	Sheppard, Dickson 133 East Ave. Los Angeles, California	(A)
Schatzel, R. A. General Cable Corp. Rome, N. Y.	(M)	Sheppard, J. R. The House on the Hill Saginaw, Missouri	(M)
Schell, Charles F. 48 Ash St. Braintree, Mass.	(M)	Sheppard, P. L. 6717 W. 33rd St. Berwyn, Illinois	(M)
Schildhauer, A. F. E. I. du Pont de Nemours & Co. Fairfield, Conn.	(M)	Sheridan, Wm. R. 1439 Kenmore Ave. Kenmore, N. Y.	(M)
Schilling, M. Brooklyn Color Works 129 Cherry St. Brooklyn, N. Y.	(M)	Shinkle, S. D. 317 Lafayette Ave. Passaic, New Jersey	(M)
Schorr, Alvin J. 5 Seaside Place East Norwalk, Conn.	(M)	Shirk, D. A. Rare Metal Products Co. Belleville, New Jersey	(M)
Schwartz, Emil W. General Electric Co. Bridgeport, Conn.	(M)	Shoaff, Paul S. Goodyear Rubber Plantations Co. Dolok Merangir E. C. Sumatra, Netherlands East Indies	(M)
Schwartz, Philip Rapid Roller Co. Federal and 26th Sts. Chicago, Illinois	(M)	Sibley, R. L. Monsanto Chemical Co. Rubber Service Division Nitro, West Virginia	(M)
Scott, David C., Jr. P. O. Box 963 Providence, Rhode Island	(M)	Sidnell, A. E. Seiberling Latex Products Co. Akron, Ohio	(A)
Scott, Winfield 326 Afton Ave. Akron, Ohio	(M)	Silver, Albert S. Crescent Co. Pawtucket, Rhode Island	(A)
Seabury, Ralph Delco-Remy Corp. Muncie, Indiana	(M)	Silver, B. R. 160 Front St. New York, N. Y.	(M)
Seigle, H. W. Elkhart Rubber Works Elkhart, Indiana	(A)	Sindler, J. J. Converse Rubber Co. Malden, Mass.	(M)
Sellers, Harry M. 13 E. Brown St. Norristown, Penn.	(A)	Slack, F. F. Corduroy Tire Co. Grand Rapids, Michigan	(M)

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| Sloan, A. W.<br>156 Edgewood Drive<br>Stowe, Ohio   | (M) | Springer, Franklin H.<br>Davol Rubber Co.<br>69 Paint St.<br>Providence, Rhode Island    | (M) |
| Smallwood, Hugh M.<br>U. S. Rubber Co.<br>Market and South Sts.<br>Passaic, New Jersey                        | (M) | Stafford, W. E.<br>131 Peel Green Road<br>Peel Green, Manchester, England                | (A) |
| Smith, Arnold H.<br>Monsanto Chemicals, Ltd.<br>Ruabon, Wrexham, Denbigshire<br>North Wales, England          | (A) | Starkweather, Howard W.<br>815 Augusta Road<br>Wilmington, Delaware                      | (M) |
| Smith, Bradley A.<br>1668 Hillside Terrace<br>Akron, Ohio   | (M) | Stavely, F. W.<br>203 Overwood Road, R. D. 7<br>Akron, Ohio                              | (M) |
| Smith, Chas. F., Jr.<br>U. S. Rubber Reclaiming Co.<br>Babcock and Hannah Sts.<br>Buffalo, N. Y.              | (M) | Stepanek, George<br>Fr. Stepanek and spol. Praha<br>Hostivar<br>Hostivar, Czechoslovakia | (A) |
| Smith, George E. P., Jr.<br>125 Morningside Drive<br>Akron, Ohio  | (M) | Stevens, M. K.<br>548 Chilton St.<br>Elizabeth, New Jersey                               | (M) |
| Smith, William C.<br>Wilton Grange<br>Kenyon, near Manchester,<br>England                                     | (M) | Stiehler, Robert D.<br>Physical Research Laboratory<br>B. F. Goodrich Co.<br>Akron, Ohio | (M) |
| Smithers, V. L.<br>2706 First Central Tower<br>Akron, Ohio  | (A) | Stillwell, C. W.<br>Dennison Mfg. Co.<br>Framingham, Mass.                               | (M) |
| Smye, Gordon R.<br>Firestone Tire & Rubber Co.<br>Beach Road<br>Hamilton, Ontario, Canada                     | (M) | Street, John N.<br>605 Sunset View Drive<br>Akron, Ohio                                  | (M) |
| Snyder, Edwin G.<br>Bowmanstown, Penn.  | (M) | Striker, Albert M.<br>Maturon Ave.<br>Lincoln Park, New Jersey                           | (M) |
| Snyder, J. W.<br>Binney & Smith Co.<br>41 E. 42nd St.<br>New York, N. Y.                                      | (M) | Stringfield, R. B.<br>229 South Normandie Ave.<br>Los Angeles, California                | (M) |
| Snyder, Joseph<br>659 Fouse Ave.<br>Akron, Ohio   | (M) | Strube, E. C.<br>Box 850<br>Trenton, New Jersey  | (M) |
| Sohon, Julian A.<br>Burroughs Library Building<br>Bridgeport, Conn.   | (M) | Sturdevant, Earl G.<br>124 Hope St.<br>Bristol, Rhode Island                             | (M) |
| Somerville, A. A.<br>(Corporation representative)<br>R. T. Vanderbilt Co.<br>230 Park Ave.<br>New York, N. Y. | (M) | Sturgis, Bernard M.<br>318 Laurel Ave.<br>Pitman, New Jersey                             | (M) |
| Speedy, Alan<br>Messrs. Binney & Smith &<br>Ashby, Ltd.<br>116 Cannon St.<br>London, E. C. 4, England         | (M) | Sturtevant, W. L.<br>Manhattan Rubber Manufactur-<br>ing Co.<br>Passaic, New Jersey      | (M) |
| Spence, David<br>P. O. Box 209<br>Pacific Grove, California   | (M) | Stutz, G. F. A., Jr.<br>Residence Park<br>Palmerton, Penn.                               | (M) |
| Sperberg, L. R.<br>Box 14, c/o Wm. Melchior<br>Stambaugh, Michigan  | (A) | Styren, Ulf<br>A/S Askim Gummivarefabrik<br>Askim, Norway                                | (A) |
|   | (A) | Swart, G. H.<br>General Tire & Rubber Co.<br>Wabash, Indiana                             | (M) |



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| Symons, R. B.<br>Canada Wire & Cable Co., Ltd.<br>Toronto, Ontario<br>Canada  | (M) | Tillinghast, P. P.<br>604 Guardian Building<br>Cleveland, Ohio  | (A) |
| Szilard, J. A.<br>740 No. Madison St.<br>Rome, N. Y.  | (M) | Tomlin, Andrew<br>Monsanto Chemical Co.<br>1012 Second National Building<br>Akron, Ohio                         | (M) |
| Takeuch, Izokichi<br>Sumitomo Kagaku Kogyo Co.,<br>Ltd.<br>"Niihama-Seizosho" Sobiraki<br>Niihama, Ehimeken, Japan                                | (A) | Torrence, Maynard F.<br>E. I. du Pont de Nemours & Co.<br>Wilmington, Delaware                                  | (M) |
| Takeuchi, S.<br>7, Komatsu Minamidori, 1-Chome<br>Hagashiyodogawaku, Osaka, Japan   | (A) | Toyada, Ryunosuhe<br>Institute of Organic Chemistry<br>Kyoto Imperial University<br>Kyoto, Japan                | (A) |
| Taylor, E. A.<br>Grasselli Chemical Dept.<br>E. I. du Pont de Nemours & Co.<br>Wilmington, Delaware   | (M) | Trafflet, F. E.<br>Pequanoc Rubber Co.<br>Butler, New Jersey  | (M) |
| Taylor, E. Folger<br>85 Damon Road<br>Medford, Mass.  | (M) | Treloar, L. R. G.<br>8 Meadow Green<br>Welwyn Garden City<br>Herts., England                                    | (A) |
| Taylor, R. R.<br>72 High St.<br>Middletown, Conn.   | (A) | Trimble, Gilbert K.<br>Midwest Rubber Reclaiming Co.<br>East St. Louis, Illinois                                | (M) |
| Teed, Earl S.<br>33 Castertown Ave.<br>Akron, Ohio  | (A) | Trumbull, H. L.<br>Box 464<br>Hudson, Ohio  | (M) |
| Te Grotenhuis, T. A.<br>724 Bulkley Building<br>Cleveland, Ohio   | (M) | Tsukamoto, Tadashi<br>c/o Mrs. Asa Aoda<br>Tanaka-Higashi-Hinokuchi-Cho-26,<br>Sakyoku, Kyoto, Japan            | (A) |
| Temple, J. W.<br>13015 East Outer Drive<br>Detroit, Michigan  | (M) | Tuley, W. F.<br>Naugatuck Chemical Division<br>U. S. Rubber Co.<br>1790 Broadway<br>New York, N. Y.             | (M) |
| Ten Broeck, W. T. L.<br>Goodyear Rubber Plantations Co.<br>Chemical Research Dept.<br>Dolok Merangir<br>E. C. Sumatra, Netherlands East<br>Indies | (M) | Turner, Joseph L.<br>Titanium Pigment Co.<br>P. O. Box 58<br>South Amboy, New Jersey                            | (M) |
| Teppema, Jan<br>B & B Chemical Co.<br>Cambridge, Mass.  | (A) | Tweed, Paul B.<br>12 Manning Ave.<br>Butler, New Jersey   | (M) |
| Terano, K.<br>Engineering College<br>Kyushu Imperial University<br>Fukuoka, Japan   | (M) | Twiss, D. F.<br>9, Somerville Road<br>Sutton, Coldfield, England  | (M) |
| Thomas, R. M.<br>Standard Oil Development Co.<br>P. O. Box 243<br>Elizabeth, New Jersey   | (M) | Uber, Jay J.<br>E. I. du Pont de Nemours & Co.<br>Huntington, Mass.   | (M) |
| Thorn, F. C.<br>Garlock Packing Co.<br>Palmyra, N. Y.   | (M) | Ulman, M. A.<br>Firestone Tire & Rubber Co. of<br>India, Ltd.<br>Mills Estate, New Queens Road<br>Bombay, India | (A) |
| Thorn, Homer Z.<br>Everett Chemical Co.<br>210 Broadway<br>Everett, Mass.   | (A) | Vacca, George N.<br>Bell Telephone Laboratories, Inc.<br>463 West St.<br>New York, N. Y.                        | (M) |

Van Cleef, Paul 7720 Woodlawn Ave. Chicago, Illinois	(M)	Washburn, C. R. Goodyear Tire & Rubber Co. of Java, Ltd.	(M)
Van de Walle, W. 857 W. Market St. Akron, Ohio	(A)	Buitenzorg, Centrum Java, Netherlands East Indies	
Varney, A. M. 46 Allston St. West Medford, Mass.	(M)	Waters, Joseph E. 610 No. George St. Rome, N. Y.	(M)
Villars, D. S. General Laboratories U. S. Rubber Co. Market and South Sts. Passaic, N. J.	(M)	Weber, Edgar N. 51 Boylston St. West Watertown, Mass.	(M)
Vodra, V. H. 1261½ So. Cloverdale Ave. Los Angeles, California	(M)	Wehmer, Fred J. Minnesota Mining & Mfg. Co. 411 Piquette Ave. Detroit, Michigan	(M)
Vogt, W. W. 189 Pasadena Ave. Akron, Ohio	(M)	Weil, Richard 728 Ellis Court Ashland, Ohio	(M)
Voigtman, E. H. Kimberly-Clark Corp. Neenah, Wisconsin	(A)	Welcher, Harold A. 143 Johnson Ave. Newark, New Jersey	(M)
Vormelker, Philip 1918 So. 10th Ave. Maywood, Illinois	(M)	Weller, S. 1033 Dempster St. Evanston, Illinois	(M)
Wakefield, H. F. Bakelite Corporation 230 Grove St. Bloomfield, New Jersey	(M)	Werkenthin, Theodore A. 3601 Second Street South Arlington, Virginia	(M)
Walker, G. B. Wilkinson Process Rubber Co., Ltd. Batu Caves Selangor, Federated Malay States	(A)	Wetherbee, Burt W. 1396 Clinton St. Buffalo, N. Y.	(M)
Walker, H. W. Box 473 Woodstown, New Jersey	(M)	Whitby, G. S. Chemical Research Laboratory Teddington, Middlesex, England	(M)
Walker, Lawrence D. 69 Delaware Ave. Freeport, Long Island, N. Y.	(M)	White, Horace C. Apt. 204 627 W. Market St. Akron, Ohio	(M)
Walton, James C. 6 Rowena Rd. Newton Center, Mass.	(M)	Whitehead, R. R. 609 Greenwood Ave. Trenton, New Jersey	(A)
Warner, A. E. C. P. Hall Co. First Central Tower Akron, Ohio	(M)	Whittenberg, J. E. 129 Dodge Ave. Akron, Ohio	(M)
Warner, R. M. 556 Lloyd St. Barberton, Ohio	(M)	Wiegand, W. B. Columbian Carbon Co. 214 44th St. Brooklyn, N. Y.	(M)
Warrell, J. E. Pharis Tire & Rubber Co. Newark, Ohio	(M)	Wiley, H. L. 443 So. University Boulevard Denver, Colorado	(M)
Warren, R. F. American Chain & Cable Co. Bridgeport, Conn.	(M)	Willey, L. M. General Electric Co. 1 River Road Schenectady, N. Y.	(M)
		Williams, C. S. 464 Cooper St. Woodbury, New Jersey	(M)

Williams, Ira J. M. Huber Corp. Drawer 831 Borger, Texas	(M)	Wright, Donald D. Hood Rubber Co. Watertown, Mass.	(A)
Wilson, J. British Rubber Research Board 19 Fenchurch St. London, E. C. 3, England	(M)	Wyrough, George Whitehead Bros. Rubber Co. Trenton, New Jersey	(M)
Winkelmann, H. A. 419 Oakdale Ave. Chicago, Illinois	(M)	Yerzley, Felix L. Rubber Chemicals Division E. I. du Pont de Nemours & Co. Wilmington, Delaware	(M)
Winspear, George G. Bell Telephone Laboratories, Inc. 463 West St. New York, N. Y.	(M)	Youmans, E. D. 59 Club Road Montclair, New Jersey	(M)
Winter, L. A. G. 134 Stibbard Ave. Toronto, Ontario Canada	(A)	Youse, Lawrence K. 254 Newhill Ave. Somerset, Mass.	(M)
Winters, Russell 110 Davis St. New Haven, Conn.	(M)	Zeller, Josef O. 5316 Devonshire St. Detroit, Michigan	(M)
Wise, Leonard G. E. I. du Pont de Nemours & Co. Experimental Station Wilmington, Delaware	(M)	Zilles, John A. 13969 Whitcomb Ave. Detroit, Michigan	(A)
Wisenburg, Ralph D. 416 So. 16th St. Coshocton, Ohio	(A)	Zimmerman, E. C. 145 No. Firestone Boulevard Akron, Ohio	(M)
Wishnick, R. I. Wishnick-Tumpeer Co. 295 Madison Ave. New York, N. Y.	(M)	Zimmerman, Elmer W. 6708 46th St. Chevy Chase, Maryland	(A)
		Zoller, Miles M. Temple Bar Building Cincinnati, Ohio	(A)

## SPRING MEETING OF THE DIVISION OF RUBBER CHEMISTRY, CINCINNATI, OHIO, APRIL 11-12, 1940

The Division had its headquarters in the Hotel Gibson. The technical sessions were held on Thursday afternoon, April 11, and Friday forenoon, April 12, with about 250 in attendance. The complete program was as follows:

1. J. McGavack and C. E. Rhines. "Correlation of Nitrogen and Ash with Total Solids Content of Latex."
2. A. R. Kemp, F. S. Malm, G. G. Winspear and B. Stiratelli. "Diffusion of Sulfur in Rubber and Its Relation to Vulcanization."
3. George L. Clark, Ernest Blaker and John M. Ball. "Hysteresis in the Crystallization of Stretched Vulcanized Rubber from X-Ray Data and the Correlation with Stress-Strain Behavior and Resiliency."
4. E. W. Booth and D. J. Beaver. "The Effect of Hydrogen Sulfide on the Rate of Vulcanization of Rubber Compounds."
5. Chas. K. Novotny and Wilbur F. Jordan. "Machine and Methods for Testing Mechanical Stability of Latex."
6. George Sackett. Report of Crude Rubber Committee.
7. S. D. Gehman and J. E. Field. "The X-Ray Structure of Rubber-Carbon Black Mixtures."
8. H. C. Jones and H. A. Yiengst. "Dilatometer Studies of Pigment-Rubber Systems."

9. Henry F. Palmer and Robert H. Crossley. "The T-50 Test Applied to Reclaimed Rubber."

10. C. S. Fuller, C. J. Frosch, and N. R. Pape. "X-Ray Examination of Polyisobutene."

11. J. M. Davies and W. F. Busse. "Dielectric Properties of Plasticized Polyvinyl Chloride."

The report of the Crude Rubber Committee, presented by George A. Sackett, was supplemented by a report of E. W. Oldham, who described a new procedure for the estimation of foreign material in crude rubber. (The report of the Crude Rubber Committee, including this supplementary material, appears elsewhere in this issue.)

On Thursday evening 300 members and guests attended the banquet held in the roof ballroom of the Hotel Gibson. The main entertainment was provided by J. E. Blackledge, magician. The Division is indebted to V. L. Smithers, Enos Baker and A. C. Eide for their efficient handling of arrangements for the banquet.

The assistance of the Cincinnati Section in partially meeting the cost of the entertainment program enabled the committee to provide this banquet at an appreciably reduced rate.

At the Business Meeting, following the papers' sessions, the Chairman, E. B. Curtis, reported the following actions of the Executive Committee:

(1) Creation of a Papers Committee to study and revise the rules for submission and publication of papers presented before the Division.

(2) Creation of a committee to study and recommend changes in the present method of election of officers.

(3) Endorsement of the formation of the fifth Rubber Group in Buffalo, the organization of which has been promoted by B. W. Wetherbee.

(4) Authorization of the publication, in the July issue each year of *Rubber Chemistry and Technology*, of a complete list of members of the Division.

The Chairman of the Auditing Committee, George Allison, reported that the annual audit of the books of the Treasurer of the Division had been made and that all accounts were in order.

The Chairman of the Membership Committee, C. R. Haynes, reported a substantial increase in new membership and urged older members to encourage the younger men in their organizations to take a more active part in the activities of the Division.

In the absence of H. L. Trumbull, Chairman of the Nomenclature Committee, the Chairman of the Division stated that the work of this committee is in progress, and that a formal report will be rendered at the Detroit meeting.

R. H. Gerke, Chairman of the Planning Committee, called on the membership for suggestions which would stimulate attendance at meetings and insure the submission of a greater number of papers. He stated further that it had been found that the consensus of opinion favored the holding of more symposia as part of future meetings. The Committee will welcome specific recommendations in this respect.

The Secretary, in the absence of Thomas Midgley, Chairman, reported for the committee promoting the election of Charles Goodyear to the Hall of Fame, that literature, such as attractive reprints of the papers presented at the Boston meeting dealing with the contributions of Charles Goodyear, together with a personal letter, will be sent to each elector in the near future. Mr. Midgley is using every possible means to secure favorable action by the Electors on the nomination of Charles Goodyear. The elections will be announced next October.

In closing the meeting, Chairman Curtis expressed his appreciation to the authors of papers for their contributions to the success of the meeting, and to all officers and members who assisted in its successful culmination.

Secretary's Report:

Total Membership, March 31, 1940.....	644
Members paid for 1940.....	515
Associate Members paid for 1940.....	129
New Members and Associate Members from August 31, 1939, to March 31, 1940 (included in above figure).....	75
Regular Members .....	51
Associate Members .....	24
Subscriptions to RUBBER CHEMISTRY AND TECHNOLOGY.....	308
Honorary Members and Exchanges.....	24

H. I. CRAMER, *Secretary.*

## BENJAMIN DAWSON PORRITT

JANUARY 26, 1884-JANUARY 28, 1940

It is with deep regret and a sense of great loss that we announce the death of Mr. B. D. Porritt, Director of the Research Association of British Rubber Manufacturers, which occurred on Sunday, January 28.

He was appointed Director of Research in March, 1920, and after a short period of initiatory work at University College, London, he established and equipped the laboratories in Croydon. His conspicuous organizing ability and wide experience enabled him to build up the Research Association to its present proud and successful position. Much of that success was due to his great faith in the value of coöperative research. He never tired of urging that the various research activities of the rubber and allied industries should be brought together, and he contributed as much as any man to the considerable unification already realized.

He was born in Manitoba, Canada, of Yorkshire parents, but was soon brought to England, his education being completed at the Croydon Whitgift School, and University College, London, where he graduated in Chemistry in 1908.

He gained valuable technological experience with the North British Rubber Co., Ltd., Edinburgh, which he joined in 1908, becoming chief chemist in 1912, and leaving only to undertake the onerous pioneer task of building up the Research Association.

He became a Fellow of the Institute of Chemistry in 1911, of the Royal Society of Edinburgh in 1917, of the Institution of the Rubber Industry in 1925, and of the Institute of Physics in 1937. He received the Colwyn Gold Medal in 1938. He was ever active in promoting the welfare of the Institution of the Rubber Industry in particular, and in addition to work on many committees, was Chairman of the Examinations Board, 1936-38, and a Vice-President from 1936 to his death.

In a personal sense, he was a splendid man, genial and lovable, with a host of friends throughout the rubber industry, and a staff at Croydon that was proud and happy in his service.

T. R. DAWSON in the *Journal of Rubber Research.*

## CHARLES REID BOGGS

NOVEMBER 22, 1883-APRIL 1, 1940

It is impossible to describe the loss which the passing of Charles Reid Boggs means to the rubber industry. An engineer and technologist of outstanding



ability, a man of keen perception, and a dynamic force in the industry during its transition from art to science, Boggs was an inspiration to all. Gifted with a logical mind and a superabundance of energy, he contributed much to the chemistry of rubber and the mechanical and electrical engineering of the rubber industry.

In 1917 he discovered the vulcanization of rubber by selenium, and later showed that remarkable properties can be obtained with this vulcanizing agent. In 1919 he patented the use of amines as accelerators, and this patent was of great aid in freeing American industry from the domination of foreign patents and in protecting the use of organic accelerators in this country. More than this, Boggs showed that accelerators improve not only the quality of vulcanized rubber but, to quote his patent, the "lasting qualities of life of a rubber product" or its "enduring qualities". This is of extreme significance, since it heralded the general use today of amines as antioxidants. In 1926 Boggs discovered that the electrical properties of rubber can be greatly improved by removing its protein. These highlights are but some of his achievements.

Boggs was born in Tennessee in 1883, and graduated in 1905 from the Massachusetts Institute of Technology, where he remained for a year as assistant in electrochemistry. He then began his long and eminent career at the Simplex Wire and Cable Company where he served as Chief Chemist from 1906 to 1917, Factory Manager from 1917 to 1929, Vice President from 1930, a Director from 1933, and General Manager from 1936. During his leadership, the company attained an outstanding position in the rubber industry.

Boggs was a member of the American Chemical Society, the American Society for Testing Materials, the American Society of Electrical Engineers, and the American Association for the Advancement of Science, and an honorary member of the British Institution of the Rubber Industry. He was a founder of the Division of Rubber Chemistry of the American Chemical Society, Chairman of the Division in 1924-1925, and a founder and a chairman of the local Boston Group of this Division.

Despite the eminence to which Boggs rose in his profession and the honors which are his due, he remained humble in spirit, and his fine sense of humor, his great courage in overcoming obstacles, and his keen discernment aroused the admiration of all who knew him.

Rubber chemists and technologists will be forever grateful to Charles Reid Boggs for his many contributions to their profession and thereby to the welfare of mankind.

J. C. W.

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## NEW BOOKS AND OTHER PUBLICATIONS

**RUBBER LATEX.** H. P. and W. H. Stevens. Chemical Publishing Co., Inc., 148 Lafayette St., New York, N. Y. 1940. Cloth, 5½ by 8½ inches, 224 pages. Indexed. Price, \$2.

This book is a reprint of the fourth edition of a paper-bound publication of the same name, issued by The Rubber Growers' Association in 1936. No new data or revisions are incorporated in the present American edition. The text portion of the book, 82 pages in length, deals briefly with the properties, composition, stabilization, concentration, compounding, processing, and applications of latex. The remainder of the book contains brief abstracts of nearly 1,000 selected British patents, covering the period 1920 to 1935. There are indexes to text, patents, and patentees. [From the *India Rubber World*.]

MANUAL DE LA INDUSTRIA DE LA GOMA. Luis Pascual Mejias Lopez. Published by *La Goma*, Calle de Moncada 4, Barcelona, Spain. 6½ x 9½ in. 362 pp. 50 pesetas. (In Spanish only.)

This manual of the rubber industry is a condensed version in Spanish of the "Encyclopedie du Caoutchouc et des Industries qui s'y Rattachent", the French manual, published in 1929 by the *Revue Générale du Caoutchouc*, the French rubber journal. Whereas the French manual consisted of various chapters devoted to miscellaneous subjects pertaining to rubber and the manufacture of rubber products, each prepared by a leading technologist familiar with the particular topic, this Spanish manual was prepared by only one author. The Spanish manual, which like the French one discusses the source, collection and application of rubber in its many different forms, was originally published some time late in 1936, and in fact carries a date-line of that year, but apparently the disturbances in Spain during the past few years have held up its receipt in this country until the present. [From *The Rubber Age* of New York.]

1939 BOOK OF A.S.T.M. STANDARDS. (IN THREE PARTS.) PART I: METALS, 1,335 PAGES. PART II: NON-METALLIC MATERIALS—CONSTRUCTIONAL, 1,250 PAGES. PART III: NON-METALLIC MATERIALS—GENERAL, 1,205 PAGES. Published by the American Society for Testing Materials, 260 South Broad St., Philadelphia, Penn. Prices (to non-members): Any one part, \$8.00; any two parts, \$15.00; all three parts, \$22.00. Each part, 6 x 9 in.

Important changes are incorporated in this latest A.S.T.M. publication. For the first time it contains *all* of the Society's specifications, whether standard or tentative. Formerly, the tentative specifications were issued in an annual volume, but the convenience of having these and the formally adopted standards in one volume led to the present combination. Another change is that the book is in three parts, instead of only two parts as before. Each part, the contents of which is indicated by the respective titles, contains a complete subject index. Three tables of contents help make the book of maximum utility. The first lists items under the general materials covered; the second gives a complete list of all the items in the part by numeric sequence; the third covers by subject the tentative standards which appear in the back portion of each part.

In all, there are 866 separate standard and tentative specifications, methods of test, definitions, etc., in the three parts, with 28 duplications. Part I has 298 items, Part II has 351, and Part III has 245. Thirty specifications, tests, definitions, etc., on rubber products appear in Part III. These cover general methods, hose and belting, gloves, matting and tape, wire and cable, cement, sponge, and hard rubber products. Practically all the specifications and tests have been reset in a new double-column format, the new style resulting in easier and better readability. The method of issuing the 1939 Book of Standards also provides that a supplement to each of the three parts be issued in 1940 and 1941. Purchasers of the book may subscribe for these supplements at the same time. [From *The Rubber Age* of New York.]

1940 INDEX TO A.S.T.M. STANDARDS INCLUDING TENTATIVE STANDARDS. Published by the American Society for Testing Materials, 260 South Broad St., Philadelphia, Penn. 6 x 9 in. 152 pp. Free on request.

Of service to anyone wishing to ascertain whether the A.S.T.M. has issued standard specifications, test methods, or definitions covering a particular engineering material or subject, the latest edition of this Index gives information on the Society's 885 standards as of January 1, 1940. All items are listed under

appropriate key-words according to the subjects they cover. As a convenience, a list is given of the specifications and tests, in numerical sequence of their serial designations. The Index is of special value in helping to locate the standards in the Society's volumes. [From *The Rubber Age* of New York.]

PROCEEDINGS OF THE 42ND ANNUAL MEETING. (VOL. 39.) Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penn. 6 x 9 in. 1350 pp. \$8.50, heavy paper binding; \$9.00, cloth; \$10.00, half-leather.

This is the first time that the A.S.T.M.'s "Proceedings" has been issued in one volume. It covers not only all of the committee reports made at the annual meeting, Atlantic City, June 26-30, 1939, but also all of the technical papers at that meeting. The committee reports not only give full details of the important recommendations on specifications and standardized test methods for materials, but in many cases include important data and information in the form of appended section-reports or papers. The report of Committee D-11 on Rubber Products, and the several papers presented at the meeting of that committee at Atlantic City last year, are of course included in the book. The Fourteenth Edgar Marburg Lecture on "Stress, Strain and Structural Damage", by H. F. Moore, precedes the technical paper section of the book. [From *The Rubber Age* of New York.]

HYDROCARBON CHEMISTRY. A General Discussion. Reprinted from *Transactions of Faraday Society*, Vol. 35, Part 8, August, 1939. Published by Gurney & Jackson, 98 Great Russell St., London, England. Cloth, 6 by 9½ inches, 286 pages. Price 12s. 6d. Postage 1s. extra.

This volume comprises the papers on hydrocarbon chemistry, together with discussions thereon, presented at the Seventieth General Discussion of the Faraday Society, held at the Imperial College of Science, London, England, April 17 to 19, 1939. The subject matter is divided into four parts: homogeneous thermal reaction of hydrocarbons; catalytic reactions of hydrocarbons; the mechanism of the technical synthesis and transformation of hydrocarbons; and olefin polymerization. In this last part considerable attention is given to the mechanism of polymerization. Results of an ozonolysis of a butadiene polymer show that in aqueous emulsion butadiene polymerizes with all the possible additive mechanisms taking place, and that the polymer consists of a highly complex mixture, in which the main carbon chains vary in their degree of unsaturation, number, and disposition of vinyl side chains, and in the extent of chain branching. It is further demonstrated that a copolymer of equimolecular quantities of butadiene and methyl methacrylate is composed chiefly of alternate units of butadiene and methyl methacrylate. The book, containing much data, represents a valuable contribution to the chemistry of hydrocarbons. [From the *India Rubber World*.]

PHYSICAL CONSTANTS OF HYDROCARBONS. Volume II. Cyclanes, Cyclenes, Cyclynes, and Other Alicyclic Hydrocarbons. Gustav Egloff. American Chemical Society Monograph Series. No. 78. Published by Reinhold Publishing Corp., 330 W. 42nd St., New York, N. Y. 1940. Cloth, 6 by 9 inches, 608 pages. Four-Volume Series. Price \$12 for Volume II.

This book is the second of a four-volume work on the physical constants of pure hydrocarbons. The first volume, published in 1939, covered aliphatic compounds. The data, arranged in tabular form, include melting point, boiling point, specific gravity, index of refraction, and additional information. [From the *India Rubber World*.]

**R.M.A. MANUAL OF RETREADING AND RECAPPING.** Published by the Rubber Manufacturers Association, Inc., 444 Madison Avenue, New York City. 8½ x 11 in. 14 pp. 10c per copy.

In the past, information regarding retreading was included in the R.M.A.'s "Manual of Tire Repairing". Because of the present importance of retreading and recapping, however, it has been deemed desirable to publish a separate manual on the subject, confining the text of the first-named manual to information on sectional repairing. The new manual gives recommended processes for retreading, recapping and top-capping, and discusses such factors as inspection, preparation, die-size selection, building, curing and finishing. [From *The Rubber Age of New York.*]

**SULFATED OILS AND ALLIED PRODUCTS.** Donald Burton and George F. Robertshaw. Published by Chemical Publishing Co., Inc., 148 Lafayette St., New York City. 5½ x 8½ in. 172 pp. \$5.00.

The chemistry, literature and analysis of sulfated oils and allied products are adequately covered in this monograph. In each case, the analysis of sulfated fatty products is preceded by a brief general outline of the various classes of compounds of this nature, of their production, and of what is known as to their chemical constitution. Subsequently, the authors discuss each proposed method for the determination of the various analytical characteristics critically, and point out where existing technique must be considered faulty. In view of the fact that our knowledge of the mechanism of the "sulfonation" process and of the products presented in "sulfated" oils or fatty acids is so very incomplete, this monograph serves a most constructive purpose. [From *The Rubber Age of New York.*]

**COMMODITIES IN INDUSTRY.** Prepared and published by the Commodity Research Bureau, Inc., 82 Beaver St., New York City. 8½ x 11 in. 720 pp. \$7.50.

Although bearing the title "Commodities in Industry", this is actually the 1940 Commodity Year Book, the second in the annual series of volumes announced by the Commodity Research Bureau last year. Like the first edition it is a capably compiled review of the commodity markets.

In addition to a discussion of the general commodity price level, from which the conclusion is drawn that a commodity price boom in the United States will be the inevitable result of the current European war, seventy-five basic commodities are individually analyzed. Charts and statistical tables support these studies, close observance of which reveal many striking similarities between price movements during the present war and the early stages of the World War.

The section devoted to "Rubber" begins with a four-page article largely devoted to a description of manufacturing tires and tubes. Then follows a brief review of the stock situation during 1939, operation of the restriction scheme, price fluctuations, the reclaimed rubber market and the rubber-cotton barter between the United States and Great Britain. The balance of the section is devoted to statistical tables and charts. [From *The Rubber Age of New York.*]

**THE TOOLS OF THE CHEMIST.** Ernest Child. Published by the Reinhold Publishing Corp., 330 West 42nd St., New York City. 5½ x 8½ in. 220 pp. \$3.50.

This is the first comprehensive story of the part played by laboratory apparatus development in the history of chemical education in America. The author, long associated with manufacturers and dealers in chemical equipment in America and abroad, including ten years of service with the house of Eimer and Amend



in New York City, concentrated his research on events and the individuals whose work played a significant part in the creation and development of chemical laboratories and apparatus in this country, rather than on the evaluation of the scientific achievements of the many who have done so much to stimulate interest in chemistry and the advancement of science. The result is an interesting, well-written tale, the telling of which has long been overdue.

The book is divided into three parts: People and Events in American Chemistry; Ancestry and Development of American Chemical Laboratory Apparatus; and Distributors of Laboratory Apparatus. In a brief chapter on Rubber Ware, the history of laboratory tubing and molded rubber stopples is traced since the early experiments of Hancock about 1823. The book has a complete subject index. [From *The Rubber Age* of New York.]



## REPORT OF THE CRUDE RUBBER COMMITTEE

PRESENTED BEFORE THE DIVISION OF RUBBER CHEMISTRY AT THE SEMI-ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, APRIL 11, 1940

The meeting of the Division of Rubber Chemistry at Cincinnati on April 11-12, 1940, marks the fifth anniversary of the establishment of the Crude Rubber Committee. The Committee wishes to express its thanks to the Chairman of the Division of Rubber Chemistry and to those members of the Division who have coöperated with it in any way. The Committee also wishes publicly to acknowledge and express its appreciation of the very excellent leadership given the Committee by its past Chairmen.

The Crude Rubber Committee this year has an enlarged membership, there now being seven regular members, whereas formerly there were five; moreover each regular member has an alternate who is familiar with the work and problems under investigation by the Committee. This increase in membership was effected to cover more completely all fields of rubber technology, and to insure that each member either be present himself or be represented by a fully qualified alternate at all meetings of the Committee.

Since this is the fifth anniversary of the Committee, it may be in order to review very briefly the work of the Committee before proceeding to a consideration of the problems now under investigation.

The Committee is very much pleased that the standard recipe for testing the rate of cure of crude rubber has been so well received and so widely adopted, particularly by technical organizations closely connected with the production of crude rubber.

Standard methods of analysis of crude rubber for copper and manganese have been published by the Committee. Both these materials have long been considered deleterious to rubber, yet up to now there has been no generally accepted method for determining their percentages in crude rubber.

Procedures for the testing of latex have been published in the *Analytical Edition of Industrial and Engineering Chemistry*, and in RUBBER CHEMISTRY AND TECHNOLOGY. The procedures do not cover all types of latex testing, and additions to these will be made from time to time.

The subject of testing the plasticity of crude rubber has been under consideration for a long time and much work has been done. As yet the Committee has not reached an agreement regarding any procedure for measuring plasticity which would allow it to be proposed as a standard method.

The Committee has also given considerable attention to the development of a recipe and test to determine the resistance to aging of crude rubber, and to the problem of determining the amount of dirt or foreign material in crude rubber.

Exchange of opinions and correspondence with rubber technologists, representing producers of crude rubber as well as manufacturers, has also been of major importance. To accomplish results of lasting value, we in this country must keep in mind the needs of other users, and we must also have regard for the

problems of the producer. It is in this field that the Crude Rubber Committee can justify its existence as much as in any other.

The present activities are a continuation of the past. The Committee meets at irregular intervals to discuss the progress of study of problems under consideration and to decide on future work.

The Committee met in Akron on January 22, 1940. This was the first meeting of the enlarged committee, and it was attended by all the members and several of the alternates. The following items were under consideration, and the report on them is given below.

#### 1. PLASTICITY

A number of the details of a testing procedure were agreed on, but the Committee felt that several points should be investigated further before publishing a tentative procedure. Publication of this procedure may be expected in the near future.

#### 2. LATEX TESTING

A test for mechanical stability of latex was discussed. This test is being studied in several laboratories, and it was decided to await the results of these studies before offering a procedure to the Division. The Committee has placed this important subject on the agenda for its next meeting, and hopes to make a report at the next meeting of the Division.

Tentative procedures for testing latex have been published, and the Committee purchased a number of reprints and distributed them to various technologists, both in this country and abroad. Any member of the Division who requires a copy of these procedures, which are published on pages 136-148 of the January 1940 issue of RUBBER CHEMISTRY AND TECHNOLOGY, and on pages 593-597 of the November 1939 issue of *Industrial and Engineering Chemistry, Analytical Edition*, should write to the Chairman of the Crude Rubber Committee.

The Committee has found that there were three errors in these tentative procedures as published.

Referring to page 595 in *Industrial and Engineering Chemistry* or to page 142 in RUBBER CHEMISTRY AND TECHNOLOGY, Equation (3b), in the section on "Determining pH in Latex," should read:

$$E_0 = E_1 - \frac{pH_1(E_1 - E_2)}{pH_1 - pH_2}$$

Referring to page 597 in *Industrial and Engineering Chemistry* or to page 146 in RUBBER CHEMISTRY AND TECHNOLOGY, in the section on "Determining Viscosity and Yield Point," Equation (1) should read:

$$K_1 = \frac{\pi R^2 g d (h_1 - h_2) \times 100}{8LV}$$

Referring to page 597 in *Industrial and Engineering Chemistry* or to page 147 in RUBBER CHEMISTRY AND TECHNOLOGY, in the section on "Determining Water-Solubles", the following corrections should be made in the first paragraph under "Details".

The third sentence should read, "Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned), and make up to within about 20 cc. of the mark".

The next sentence calls for 1 *N* sulfuric acid. This should be 0.1 *N* sulfuric acid.

### 3. PACKAGING

Carefully made crude rubber cannot reach the consumer without contamination by foreign material unless it is enclosed in a suitable package which prevents the entrance of dirt. A tightly pressed bale, wrapped in treated hessian fabric, has been generally agreed as a more satisfactory package from this standpoint than venesta cases, but such bales have serious disadvantages.

A method of packing smoked sheet in a rubber wrapper appears to be a distinct improvement, and the Committee would like to have all members read the description of this type of package as given by D. E. Andrews on pages 33-37 of the March 1940 issue of the *India Rubber World*. The package described has considerable merit, and deserves serious consideration.

The present shortage of wooden cases may force the more general use of the bale as a standard package, and it would be advantageous to the crude rubber consumer to have the better grades packed in a container which would more satisfactorily keep the rubber as clean as it was when it left the plantation.

### 4. SAMPLING

All tests of rubber properties, such as rate of cure, plasticity, resistance to aging, and presence of deleterious materials require the use of single small samples. Crude rubber is not adapted to easy drawing of samples, and therefore great care must be exercised to get a truly representative quantity on which to base judgment of the whole lot under examination.

No standard procedure for sampling rubber for analysis of its technical properties has been proposed. The Committee now has this subject under its careful consideration, and will welcome suggestions or ideas from any members of the Division of Rubber Chemistry who may have done work along these lines.

### 5. RESISTANCE TO AGING

The Committee reported at the meeting in the spring of 1937 that the initial investigation of the subject of aging resistance had resulted in a mass of conflicting data. The subject has been reopened, and is now receiving further attention from the Committee.

The Committee is trying first to find whether a practical compound, tested by an accepted standard aging test, will show that crude rubber, free from deleterious substances, will show variation in its aging by the test. The test will also have to reveal the presence of deleterious substances. At present, the Committee has no definite information whether rubber varies in this way, and will welcome any information along this line from anyone who has had experience with such rubber.

### 6. RATE OF CURE

Since publication of the standard recipe, we have had a number of inquiries from various places as to what should be considered a good rate of cure for rubber.

The Committee was established to bring together the ideas of the rubber technologists in the United States regarding crude rubber, and to convey these ideas to technologists working on crude rubber in other countries. All mention of standards of quality and allowable limits of variation of any property has

been deliberately and carefully omitted, since the Committee is empowered only to set up a test and not to apply it. The Committee does not wish anyone to consider it as a group for setting up market standards.

At the meeting of the Division of Rubber Chemistry held in April 1939, the Crude Rubber Committee presented some standards which were proposed by the London Advisory Committee for Rubber Research. At that time, the American Crude Rubber Committee expressed itself as in agreement with the principle of setting standards for crude rubber, but for the reasons stated above, the American Committee could neither approve nor disapprove the standards and limits proposed.

The Crude Rubber Committee has felt, however, that publication of data obtained from the use or application of any of its standard formulas or procedures would be of interest and possibly of value to technologists, both in the United States and abroad, by showing the actual results obtainable from such procedures and thereby stimulate further interest in their use and application.

With this in mind, the Committee considered publishing further information on the variability of rubber with respect to its rate of cure.

In the report of the Committee given in April 1936, data on the rate of cure of smoked sheet were given to show the extent to which rubber varied, as revealed by the standard recipe. The tests were, however, those of selected samples and might not represent the degree to which the regular run of production might vary. The Committee decided that information on this latter point would be of value.

To show more clearly the variability of rubber, it was desirable to establish a single basis of comparison, as the introduction of a second basis or variable would complicate the picture to such an extent that confusion would result.

The rate of cure of rubber in the standard recipe can be judged by using definite properties at any of the specified cures. It is necessary, however, to set a single cure and a particular property of that cure, if simplification of testing and accuracy of judgment are to result. After careful consideration, the 40-minute cure at 126° C (260° F) was selected as satisfactory. Shorter cures are apt to exaggerate variation and longer cures repress it.

Up to the present time, the Committee has suggested that readings of the load at elongations of 500, 600 and 700 per cent be taken and recorded, as well as the load at break and the ultimate elongation. The 500 per cent modulus does not show a great deal of variation, as the load is always small. The 600 per cent modulus is, however, fairly good and has an advantage over the 700 per cent modulus in that the reading is slightly easier to make with a single observer.

It does not, however, offer the sensitivity of the 700 per cent modulus. Ultimate tensile strength does not truly reflect the stiffness of the stock, and its value is seriously affected by a number of factors, such as the machine used, the dimensions and shape of the test-strip, etc., as shown in the literature.

Taking all things into consideration, the Committee suggests that if the rate of cure is to be compared at a single cure and modulus, the 40-minute cure at 126° C (260° F) and the modulus of 700 per cent be used. This suggestion is made without prejudice to any other standards now used, and without claiming that such a single cure and modulus exactly reflect the behavior of the rubber at other cures and elongations. The Committee does feel that it is desirable to set such a single set of conditions, and that reference to such conditions as standard is advantageous.



A considerable volume of data obtained in factory testing of smoked sheet was made available to the Committee. The only point recorded in these tests was the 700 per cent modulus at the 40-minute cure at 126° C (260° F). The results have been assembled in a distribution curve, as shown in Figure 1.

The total number of tests was 16981, and the actual average modulus at 700 per cent elongation was 99.0 kg. per sq. cm. (1410 lbs. per sq. in.). The average deviation (A.D.) was 10.0 kg per sq. cm. (142 lbs. per sq. in.). The standard deviation was 12.6 kg. per sq. cm. (179 lbs. per sq. in.). According to statistical theory, the values within the range of the standard deviation comprise seventy per cent of the total. In other words, seventy per cent of the large amount

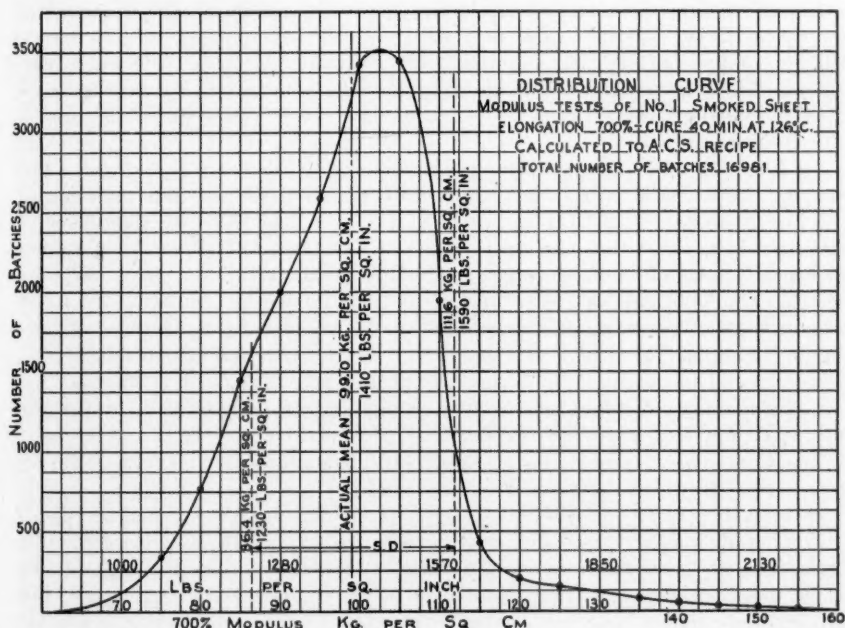


FIG. 1.

of rubber tested in this survey had a 700 per cent modulus value between 86.4 and 111.6 kg. per sq. cm. (1230 and 1590 lbs. per sq. in.). The extreme values found were 60.0 and 155.0 kg. per sq. cm. (850 and 2200 lbs. per sq. in.).

These data are presented merely to show the distribution of the 700 per cent modulus value obtained by testing a large amount of No. 1 ribbed smoked sheet passing through a single factory and tested under the conditions existing in that factory. The samples were taken from blended batches after plasticizing. If others have records of tests of rubber made on a large scale so that the data can be analyzed statistically, the Committee would be very glad to receive whatever information is available. It is also hoped that the presentation of these data may stimulate others to investigate this property, and in this way our information may be greatly increased.



## 7. DETERMINATION OF FOREIGN MATERIAL

The Crude Rubber Committee has given considerable serious attention to the determination of foreign material in crude rubber. The usual method of judging the proportion of foreign material in a given lot of rubber is to draw several samples of the rubber and visually compare it with a given standard. Such a method has been used for years for grading on the market, but it cannot be considered as more than comparative. As a means of judging whether a given lot of rubber can be used directly in the manufacture of rubber products, such as inner tubes, where a high degree of freedom from contamination is required, there is no question but that the visual inspection of a sample is of little practical value.

In undertaking this work of developing a test for determining the amount of foreign material in crude rubber, it has not been the purpose of the Crude Rubber Committee to bring out a test which would be a substitute for, or replacement of, the method of market grading. The Committee is concerned only with a test which can be used by rubber technologists to determine the dirt in any grade of rubber.

Two methods of determining foreign material have been considered. The first method is based on solution of the rubber in benzene and determination of the foreign material by filtration, washing and weighing. The disadvantages of this method are first that the use of a sample of even 20 or 30 grams of rubber requires the handling of a large volume of inflammable and toxic solvent; secondly, the determination is tedious because of the viscous solution; and third, the small size of sample renders duplication difficult because a difference of only one or two grains of sand makes an appreciable difference in the results.

The second method is based on a factory process of cleaning rubber. It has the disadvantage of requiring factory equipment, and so is not universally adaptable, nor is it so precise as a method carried out completely in a laboratory.

The Committee presents this method of determining foreign material merely as a procedure which it feels is of interest and value.

It may require modification to adapt it to the equipment and needs of various crude rubber consumers, but the essential idea of the test can probably be worked out in most factories. The most advantageous use of rubber of any grade depends in part on our knowledge of the properties of that grade, but further than that, a knowledge of the properties of a given lot of rubber enables the user to get the maximum value from it. This test is proposed with this idea in mind, and is practical rather than scientific.

### *Procedure for Estimation of Foreign Material in Crude Rubber*

A regular factory washing mill is used (see Figure 2). The size of the rolls, their speeds, and the type or depth of grooving are not specified, since there are so many variations of these particular items on satisfactory washing equipment that the Committee could not work out or specify any particular size, speed or type. The only requirement is that the equipment must do a satisfactory job of washing rubber and do this in a fairly efficient manner.

Just below the rolls of the washer is the usual perforated pan. This catches the larger particles of rubber which are broken off, and it also protects the screens from damage. Below this perforated pan is a removable pan which has extension sides to prevent any water from escaping before it has passed through the removable screen system, which is placed at the lowest point of the removable pan. The area of the screens depends on the size of mill and the volume of

water used, and should not be too large to handle easily. A size found practical for use on a 40-inch wash mill is 15 inches wide and 20 inches long.

The screen system is composed of two separate screens, placed one above the other, with a space of about two inches between them.

It is recommended that the top screen be 50-mesh, with openings approximately 0.01 inch in diameter. The lower screen should be 100-mesh, with openings 0.0059 inch in diameter.

The screen system shown in Figure 2 does not show the lower screen, which is directly below the screen which is visible.



FIG. 2.

The following procedure is recommended for carrying out the test, although, as stated before, different conditions may require alteration or modification.

With a carload as a unit of test, select 20 bales or cases and cut approximately 50 pounds or less from each bale or case, cutting across the edge so that a part of each sheet is included in the portion removed.

Take the 1000-pound (approximate) sample to the washer fitted with the screens described above. With the washer well opened, pass the pieces through to sheet them out preparatory to washing.

Care must be taken that, after selecting the samples, they are not exposed to the danger of picking up dirt in the factory from the floor or from other rubber, since contamination from this source would, of course, render the results meaningless.

After cracking the samples, set the rolls to such an opening that the finished rubber is  $\frac{1}{4}$  inch thick after the last passage through the washer. Pass the rubber through the rolls six or more times, doubling the rubber on itself each time. Adjust the water flow so that it passes away through the screen system readily, using as much water as is practicable. The amount of washing will depend on the mill itself, and the operator will have to determine the exact procedure to obtain satisfactory results on his own equipment.

While it may be argued that occasionally lots of lower grade rubber may be found which require more than the standard number of passes set for that grade to remove all dirt, the use which the operator wishes to make of the test determines how well or how completely he desires the washing to be.

After the washing is completed, flush the mill and pans with a hose to force all foreign material onto the screens. Remove the screens and take to a laboratory for completion of the test.

Wash both screens into a suitable container. Much of the material will sink to the bottom, but some rubber particles with foreign material adhering to them, together with some of the wood and bark, will float.

Pour the floating material from the container through a 20-mesh screen held over a 100-mesh screen. This 100-mesh screen need not be the same one used at the washing mill, but preferably a smaller one, which is more convenient to handle in the laboratory. The 20-mesh screen catches the rubber particles with adhering foreign material, and allows the wood and bark to pass through to the 100-mesh screen. Examine the material on the 20-mesh screen, pick off any large pieces of wood or bark and place them with the material on the 100-mesh screen.

Dry the material retained on the 20-mesh screen at a low temperature (below 50° C) to avoid making the rubber sticky. After drying, rub this material gently over a coarse screen (16-20 mesh) to loosen adhering foreign material, and catch it on the 100-mesh screen used above.

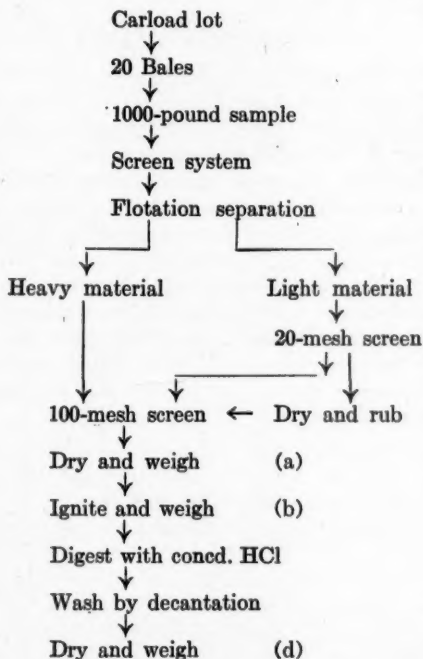
Pour the material in the original container through this 100-mesh screen, and rinse all the heavy substances from the bottom onto the screen.

The 100-mesh screen now contains all the foreign substances found in the 1000-pound sample which are over 100-mesh in size, the rubber having been completely removed. These foreign substances consist of wood, straw or fuzz from the container in which the rubber was shipped, iron scale from the washing mill, and sand, bark and wood in the rubber when packed. Except by visual examination, wood from packing cases cannot be distinguished from wood entering the rubber during manufacture.

Wash the residue on the 100-mesh screen with water, dry at 100° C and weigh; this weight is recorded as (a). Ignite, first at low heat and finally in a muffle, cool and weigh; this weight is recorded as (b). The loss (a-b) is considered to be bark, wood, straw or fuzz and is recorded as (c).

Digest the residue after ignition in concentrated hydrochloric acid in a beaker covered with a watch-glass, the beaker being placed on a steam bath for several hours or until all iron is dissolved. Wash the contents of the beaker several times by decantation with distilled water, and dry in an oven at 100° C; the weight is recorded as (d). The loss in weight is considered as iron scale

from the washing mill, not as dirt in the rubber. In tabular form, the procedure is as follows:



Foreign material in 1000 pounds of rubber:

Wood, bark, straw or fuzz = (a) - (b) = (c)

Sand = (d)

Total foreign material = (c) + (d)

To show some results which have been obtained by the test, the following data are given below. These figures are not presented as standards for the various grades and certainly are not to be interpreted as such, but are merely the results of some tests made by the given procedure.

	Size of each sample 1000 pounds		
	Total dirt (grams)	Volatile (grams)	Sand (grams)
No. 1X Ribbed smoked sheet .....	3.2	1.9	1.3
No. 1 " " " .....	4.5	2.5	2.0
No. 3 " " " .....	14.4	4.4	10.0
No. 4 " " " .....	18.9	4.2	14.7
No. 5 " " " .....	44.3	14.0	30.3
No. 2 Brown crepe .....	63.7	12.9	50.8
	133.1	48.1	85.0
No. 3 Amber blanket .....	22.3	8.5	13.8
	13.8	2.9	10.9
	12.2	6.2	6.0
	142.3	62.4	79.9
No. 4 Brown crepe .....	164.4	54.2	110.2

These data show that different shipments or lots of the same grade of rubber may contain different quantities of foreign material.

#### CONCLUDING REMARKS

The Crude Rubber Committee presents this report with the hope that all members of the Division of Rubber Chemistry will consider with serious attention all the points covered, and if anyone wishes to offer suggestions, comments or criticisms, he should do so by writing directly to the Chairman or any of the Committee members. The same applies to questions on any of the items. The Committee is particularly anxious to have comments on procedures already offered, including the test for foreign material described above.

The task of drawing up tests or procedures for use by all technologists interested in crude rubber is not an easy one, and although every effort is made to draw up these procedures so that they will be of general utility, without the interest and help of many members, the Committee can neither accomplish the best results nor fully achieve its purpose. Much remains to be done, but with the continued coöperation of the officers and members of the Division, the tasks will be accomplished.

G. A. SACKETT, *Chairman*  
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# TENSILE TESTS OF PLANTATION RUBBER \*

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The problem of the sale of plantation rubber on a basis of quality rather than merely by superficial appearance is once more a current topic. An article by Bocquet (cf. RUBBER CHEMISTRY AND TECHNOLOGY 12, 1 (1939)) discussed this paradoxical situation in which the planters find themselves, for, to be able to sell their product on the open market, they are obliged to lower the intrinsic quality of the rubber.

This abnormal situation cannot continue indefinitely, or at least this seems to be the opinion of the majority of technologists who have studied the subject. It will be necessary to abandon the sale of rubber by superficial appearance and, instead, sell it on a basis of quality. In bringing about this change, it will be absolutely necessary to establish a testing procedure on the rubber plantations which is simple and precise, and is of such a character that the results obtained in the Far East can be reproduced, at least in an approximate way, by the laboratories of the rubber manufacturers and conformity to sales specifications thereby checked.

The first attempt to develop a general technique for testing rubber was the publication in 1930 of a study by the Physical Testing Committee of the Division of Rubber Chemistry of the American Chemical Society, entitled "An Outline of Tentative Standards Laboratory Procedure for the Preparation and Testing of Rubber Samples". Efforts directed to the same end by Committee D-11 on Rubber Products, of the American Society for Testing Materials, should also be mentioned. The specifications drawn up as a result of these studies have not, however, even yet been adopted by all consumers in the United States and Europe. The specifications were, on the other hand, accepted by the Crude Rubber Committee of the Division of Rubber Chemistry of the American Chemical Society, and were supplemented in 1936 by specifications for chemical products to be used in the test mixtures (cf. *Industrial and Engineering Chemistry, News Ed.*, 14, 215 (1936)).

## SPECIFICATIONS OF THE CRUDE RUBBER COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY

The specifications proposed by the Crude Rubber Committee can, in the opinion of the present author, be used as a basis for the establishment of a final set of specifications for testing the tensile properties of plantation rubber.

But in viewing the problem solely from the point of view of the planter, who must make the tests under conditions prevailing in the tropics and with the aid of native workers, certain exceptions must be taken to the specifications.

(1) The method of the Crude Rubber Committee specifies the use of relatively expensive and complicated vulcanizing equipment, whereas similar results can be obtained with equipment which is more rugged and is simpler to install and operate, e. g., an autoclave instead of a press.

\* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 16, No. 10, pages 365-374, December 1939.

(2) Some of the specifications of the Crude Rubber Committee do not conform to the working conditions of laboratories in the tropics.

(3) The method of the Crude Rubber Committee makes it difficult to carry out the tensile tests because a dumb-bell test specimen is specified instead of a ring test-specimen.

(4) The method of the Crude Rubber Committee lacks precision in certain steps of the procedure, and this makes it impossible to obtain reproducible results in different laboratories with the same rubber when the method is followed strictly.

In the present paper these different points will be discussed and several modifications of the specifications of the Crude Rubber Committee will be proposed.

#### TESTING CONDITIONS IN THE LABORATORY OF THE TECHNICAL SERVICE DEPARTMENT OF THE SOCFIN COMPANY

Before dealing with this subject, it seems well to describe in detail the standard conditions of testing used in the Socfin laboratory, on which the present study is based.

(1) *Standard Mixture*.—The batch to be mixed weighs 221 grams, and is of the following composition:

Rubber .....	200
Sulfur .....	7
Mercaptobenzothiazole .....	1
Stearic acid .....	1
Zinc oxide .....	12

All the ingredients in this formula conform to the specifications of the Crude Rubber Committee, and are added to the rubber in the following order:

Mercaptobenzothiazole  
Zinc oxide  
Stearic acid  
Sulfur

#### (2) *Preparation of the Unvulcanized Mixture*.—

Speed of mill rolls: 24/18 rev. per min.

Temperature of mill rolls: 65° C.

Distance between rolls: 0.35 mm. (0.014 inch).

Plasticization of rubber: 2 minutes.

Addition of ingredients: 3 minutes.

Blending—6 passes, according to the specifications of the Crude Rubber Committee, with the rolls together: 3.5 minutes.

Calendering: 4 alternating passes with distance between rolls 0.70 mm. (0.028 inch).

#### (3) *Conditioning of the Unvulcanized Mixture*.—

24 hours in the open air under the conditions prevailing in the laboratory.

Temperature varying from 25° to 32° C (mean 28° C).

Humidity varying from 62 to 78% (mean 66%).

(4) *Vulcanization*.—In an autoclave, in open steam, at a temperature maintained at 126.7° C, with time of vulcanization 40 minutes, counted from the moment when the temperature of 126.7° C is reached (in 2-minutes) to the moment when the steam is shut off. Discharge of steam and opening of the autoclave: 3 minutes.

(5) *Conditioning of the Vulcanizate.*—24 hours under the same conditions as for the unvulcanized mixture.

(6) *Tensile Test.*—This test is made on a Schopper machine, with ring test-specimens cut from the vulcanized product. Rate of stretching: 400 mm. per minute. The measurements include modulus at 550 per cent and at 700 per cent elongation and tensile strength and elongation at rupture.

(7) *General Notes.*—Rubber ring test-specimens containing blisters or air pockets are rejected, and a new mixing is made if 50 per cent of the test-specimens are imperfect in this way. In studying the influence of any particular factor, only this factor is varied, all other conditions are maintained constant.

With these few facts as a basis, the main subject of this work can be discussed.

### SIMPLIFICATION OF THE LABORATORY EQUIPMENT

#### EQUIPMENT NECESSARY FOR CARRYING OUT TESTS IN ACCORDANCE WITH THE CRUDE RUBBER COMMITTEE SPECIFICATIONS

To be in a position to carry out tests in conformity with the specifications of the Crude Rubber Committee, the following laboratory equipment is necessary.

(1) A rubber mixing mill, with rolls 6 inches in diameter and 12 inches long; with circulation of hot water at 70° C; with speed of slow roll of 24 rev. per min., speed of fast roll of 33.5 rev. per min., and friction ratio of 1:4.

(2) A press for vulcanizing.

(3) Equipment for storing unvulcanized and vulcanized mixtures under standardized conditions. (The specified temperature of 27.6° C and 45% humidity are different from the conditions ordinarily prevailing in the tropics.)

(4) A tensile testing machine (the Scott machine is used everywhere in the United States).

(5) A boiler for supplying steam for the equipment.

(6) Hydraulic equipment for the vulcanization press.

(7) Various accessories, such as a precision balance for weighing the ingredients, moulds for vulcanizing, pyrometers and thermometers for controlling temperatures, a standard cutting die for dumb-bell test-specimens (or a machine for cutting out ring test-specimens), and an instrument for measuring the thickness of test-specimens.

The enumeration of these details makes it evident that the equipment necessary for a laboratory simply to make tensile tests of rubber requires a considerable outlay of money, to say the least. Moreover, this equipment is somewhat complicated, since it is necessary to have available:

(1) A supply of steam for vulcanization and for heating the water.

(2) A source of electric power (or some other source of mechanical energy).

(3) Circulating water.

(4) A source of hot water (at 70° C for the mill rolls).

(5) A source of hydraulic pressure for the vulcanization presses.

If the sale of rubber is to be established with any degree of success on a basis of quality, it must be possible for laboratory tests of rubber to be made by the native producers, whose technical knowledge and material equipment are naturally limited. Hence every justifiable simplification of laboratory equipment and operation of the equipment are of the greatest importance.

#### AUTOClave OR VULCANIZATION PRESS

The first step in the right direction for the plantations, a step which can be taken without detriment to the results, is to replace the vulcanization press by

an autoclave. This reduces the cost of equipment and also simplifies the equipment from the operating point of view, *i. e.*, it obviates a hydraulic system, and an autoclave is easy to manipulate.

We have had an opportunity to compare the results of tests made on the same samples vulcanized in an autoclave and in a press. The results are identical for the mixture of the composition specified by the Crude Rubber Committee.

When a press is used, the test-specimens are naturally less likely to contain blisters or air pockets, and consequently the tensile strengths of the various test-specimens of any particular vulcanizate show smaller deviations than do test-specimens from a sample vulcanized in open steam. When an autoclave is used and care is taken in preparing the samples, the number of air bubbles is, nevertheless, relatively small.

#### EQUIPMENT FOR STORAGE OF UNVULCANIZED AND VULCANIZED MIXTURES

A further simplification, although of a more debatable character, is the elimination of equipment for storing samples before and after they are vulcanized.

It has been demonstrated that the conditions of storage, including light, temperature and humidity, influence to a marked extent the results of the tests, and the specifications of the Crude Rubber Committee are very definite on this subject.

Regarding the effect of light, it can be said that in the equatorial part of the tropics, such as Malaya, the temperatures of the laboratories vary from 25° C to 32° C, and the humidity from 62 to 78 per cent. In Indochina these variations are greater, the temperature varying from 20° to 38° C and the humidity from 50 to 95 per cent.

However, during working hours, *i. e.*, from 8 A.M. to 4:30 P.M., deviations from a temperature of 28° C and humidity of 66 per cent are relatively small, and can be disregarded in ordinary testing. To determine the parts played by these factors, the experiments described in the following sections were carried out.

#### INFLUENCE OF TEMPERATURE

Six unvulcanized rubber mixtures and six vulcanized rubber mixtures were stored for 24 hours under the following temperature conditions:

14-15° C .....	4 mixtures (2 of each type)
27-28.5° C .....	4 mixtures (2 of each type)
40° C .....	4 mixtures (2 of each type)

The average results of tests on 16 ring test-specimens under each of the above conditions are recorded in Table I. These results show that the vulcanized mixtures were more sensitive to the temperature of storage than were the same mixtures before vulcanization. In general deviations in the measurements may be expected to reach  $\pm 5$  per cent for the extremes of temperature of a laboratory. Since, on the other hand, the temperature of storage specified by the Crude Rubber Committee, *viz.*, 82° F (27.6° C) differs but little from the ordinary temperature of laboratories in the tropics (25° to 30° C) the influence of temperature can be disregarded in ordinary commercial or routine testing.

TABLE I

Temp. of testing	Unvulcanized mixtures			Vulcanized mixtures				
	Modulus at 550%	Modulus at 700%	Tensile strength	Maximum deviation	Modulus at 550%	Modulus at 700%	Tensile strength	Maximum deviation
14-15° C	15.0	31.5	91.0	+3%	13.25	25.5	82.0	-6%
27-28.5° C (labora- tory)	14.75	30.5	89.5	control	13.75	27.0	83.0	control
40° C	14.75	30.25	88.5	-1%	14.0	28.0	84.0	+4%

TABLE II

Atmospheric humidity (%)	Unvulcanized mixtures			Vulcanized mixtures				
	Modulus at 550%	Modulus at 700%	Tensile strength	Maximum deviation	Modulus at 550%	Modulus at 700%	Tensile strength	Maximum deviation
25-30	14.5	29.0	89.5	-5%	15.75	34.0	82.0	-10%
62-78	15.0	30.5	92.5	control	16.25	34.5	90.0	control
83-97	15.5	33.0	94.0	+8%	16	34.5	92.0	+2%



## INFLUENCE OF ATMOSPHERIC HUMIDITY

Six unvulcanized and six vulcanized mixtures were prepared and were stored for 24 hours under the following conditions.

- 4 mixtures (2 of each type).....in air dried to a humidity of 30-35%.
- 4 mixtures (2 of each type).....in the air of the laboratory, *i.e.*, 60-78%, with an average of 66% humidity.
- 4 mixtures (2 of each type).....in air almost saturated by water, *i.e.*, 97% humidity at the beginning of the test and 83% at the end.

The average results of tests of sixteen ring test-specimens for each condition are recorded in Table II.

These results show that the humidity of the air during storage of the various mixtures had considerable influence on the results.

Since the average humidity of the air in the Socfin laboratory is around 66 per cent, *i. e.*, about 50 per cent higher than the average humidity specified by the Crude Rubber Committee (45 per cent), differences must be expected in the results obtained with the same rubber when tested by the same specified procedure in Malaya, Europe and the United States, unless some sort of air-conditioning equipment is used for storage of samples.

Such an installation would certainly be justified, and perhaps indispensable, in research work. On the other hand, if a tolerance of 5 to 7 per cent difference in the modulus and tensile strength values is considered satisfactory for commercial routine testing, an installation of this kind is not necessary.

In conclusion, then, the laboratory equipment necessary for testing plantation rubber on a commercial scale can be simplified in two ways:

- (1) By the use of an autoclave instead of a press.
- (2) By elimination of special conditioning chambers for unvulcanized and vulcanized samples (which would be necessary if the conditions specified by the Crude Rubber Committee were to be fulfilled in the tropics), provided that differences of 5 to 7 per cent in the results obtained in the tropics are satisfactory as a tolerance.

## SPECIFICATIONS OF THE CRUDE RUBBER COMMITTEE INCOMPATIBLE WITH THE WORKING CONDITIONS OF LABORATORIES IN THE TROPICS

The specifications of the Crude Rubber Committee require: (1) that the temperature of the mixing rolls be maintained at 70° C (158° F); (2) that the distance between the rolls be governed by the size of the batch, and (3) that the temperature at which the tensile tests are made be 82° F (27.6° C).

(1) *Temperature of the Mixing Rolls.*—The specifications of the Crude Rubber Committee fix this temperature at 70° C.

The influence of the temperature of the mixing rolls is undeniable. The results of some tests with the mercaptobenzothiazole recipe of the Crude Rubber Committee are reproduced graphically in Figure 1 to show the extent of this influence.

However, under the working conditions prevailing in the tropics, it has been found to be difficult to mix batches with the rolls at 70° C because of adhesion of the stocks to the rolls. The tendency to adhere to the rolls is probably attributable to the excessive humidity of the air, which averages 66 per cent.

If the procedure is to be simplified, a mill roll temperature not exceeding 65° C must be accepted as satisfactory. According to information which we

have received, some of the other laboratories in the Far East have, like the Socfin laboratory, been obliged to limit themselves to a mill roll temperature of 65° C.

**Spacing of the Rolls.**—The specifications of the Crude Rubber Committee define the spacing of the mill rolls as a function of the volume of the batch. Without challenging the merits of this specification, it may merely be observed that such a procedure gives too much latitude to the operator, including the temperature of the batch, the spacing of the rolls, etc., a practice to be avoided among native planters.

We prefer to fix the size of batch at a constant value, *viz.*, 200 grams of rubber plus the accessory ingredients. This mixture is large enough to fill a mill and to give eight ring test-specimens. For any weight of a specified type of mixture, which in the case of the mercaptobenzothiazole mixture of the Crude

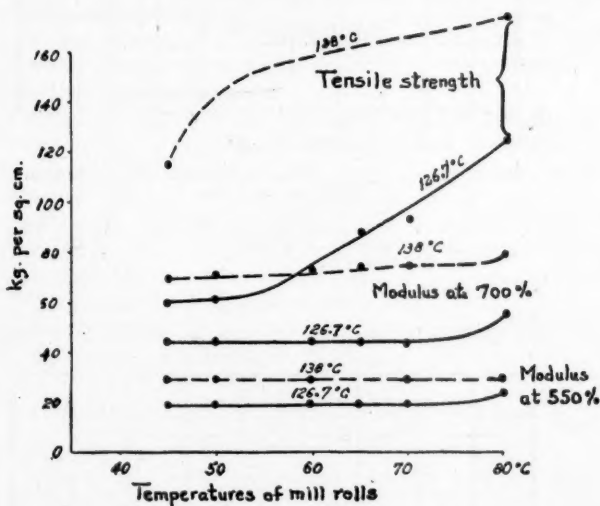


FIG. 1.—Influence of the temperature on the mill rolls.

Rubber Committee would be a batch weighing 221 grams, there is a corresponding definite time of each operation and, as will be shown later, it is important to prescribe these conditions in definite terms.

Since the weight of batch is relatively small, the question of the spacing of the mixing rolls is of secondary importance. To show this, the results of tests with a 221-gram batch of the Crude Rubber Committee formula, with various spacings of the mill rolls, are given in Figure 2. These graphs show that the influence of this factor is insignificant under the conditions in question. Nevertheless, to make the mixing operation an exact procedure, we have set the spacing of the rolls at 0.014 inch (0.35 mm.) for mixing and at 0.228 inch (0.70 mm.) for calendering. With the equipment of the Socfin laboratories, these figures correspond to 2.5 and 4 turns of the adjusting winch on the rolls, so that the operation is very simple.

(3) **Temperature for Making Tensile Tests.**—The specifications of the Crude Rubber Committee prescribe a temperature of 82° F (27.6° C), with a tolerance of 1-2° F, for the laboratory during testing.

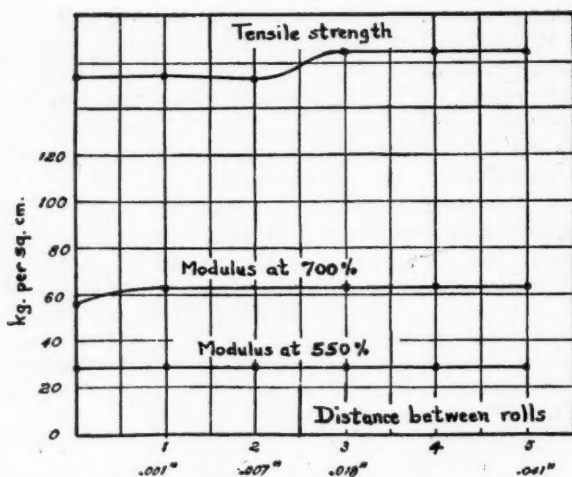


FIG. 2.—Effect of the spacing of the mill rolls on batches weighing 221 grams.

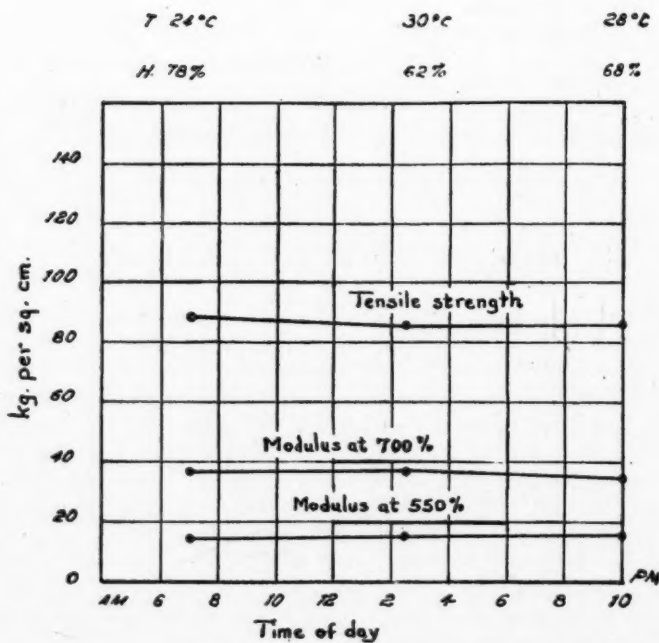


FIG. 3.—Influence of the temperature on the laboratory on the results of tests.

Under normal conditions, the temperature of the Socfin laboratory increases from 24° C in the morning to 30° C at full heat of the day, *i. e.*, it is practically impossible to conform to the working conditions recommended by the Crude Rubber Committee.

The following tests were carried out to determine the influence of this temperature in making tensile tests.

Three mixtures were prepared in an identical way and were tested under the following conditions.

- (1) At 28° C, with 68% humidity, at night.
- (2) At 24° C, with 78% humidity, in the morning.
- (3) At 30° C, with 62% humidity, at about 2:30 P.M.

Figure 3 shows that during working hours the temperature of the laboratory has only a slight influence on the results, and can be disregarded in testing plantation rubber commercially.

In summary, it is believed that if the testing procedure of the Crude Rubber Committee is to be adapted to working conditions in the tropics, it is advisable:

- (1) To limit the temperature of the mill rolls to 65° C.
- (2) To prescribe a definite weight for the batch, which should not exceed 250 grams, *e. g.*, in the case of the mercaptobenzothiazole recipe of the Crude Rubber Committee, the weight should be exactly 221 grams, corresponding to 200 grams of actual rubber.
- (3) To prescribe the spacing of the mill rolls in a way which will make it simple to operate; as the influence of this spacing is almost insignificant for batches smaller than 250 cc., the establishment of an operating procedure can be left to the discretion of the individual laboratories.
- (4) To extend the allowable limits of the laboratory temperature to a range of 25° to 30° C, instead of fixing it at 27.6° C.

#### SIMPLIFICATION OF THE TESTING PROCEDURE

It appears, *a priori*, that in the commercial testing of plantation rubber, every possible simplification in the testing procedure which does not affect the results adversely should be adopted. In our opinion, the procedure specified by the Crude Rubber Committee may be simplified in the following two ways:

- (1) By the use of ring test-specimens instead of dumb-bell test-specimens.
- (2) Perhaps by utilizing masterbatches for preparing the rubber mixtures.

#### TESTS WITH DUMB-BELL AND RING TEST-SPECIMENS

Certain "theoretical" justifications for dumb-bell test-specimens will not be discussed at this time, for the question is of interest only from a practical point of view, *i. e.*, the testing procedure in the two cases.

For pure research, dumb-bell test-specimens seem, *a priori*, more justified, for the tension is distributed uniformly over the cross-section of the test-specimen and parallel to the direction of its calendering, rupture of the specimen normally takes place in the narrow part of the specimen, etc.

From the standpoint of practical testing, this means that:

- (1) Before proceeding to the calendering operation, the mixed bath should be perfectly distributed across the full width of the mill rolls.
- (2) Calendering should be uniform throughout the length of the sheet.
- (3) The calendered sheet should be placed in the cavity of the mould in such a way that the direction of the calender grain is the same as that of the cutting out of the dumb-bell test-specimens.

(4) The test-specimens should be cut out by the die in a direction corresponding exactly to the direction of calendering.

(5) The test-specimen should be marked very accurately and placed very accurately in the testing machine.

The mere enumeration of all these details of operation is sufficient to justify our doubt about the possibility of obtaining the same results with the same rubber by different operators in different laboratories.

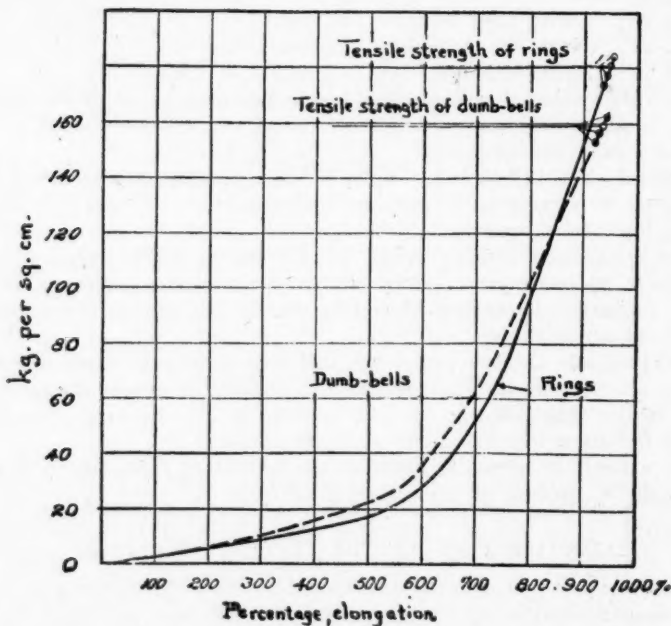


FIG. 4.—Comparison of tests with dumb-bell and ring test-specimens.

The method of testing with ring specimens, which is preferred on the European continent, has the enormous advantage of simplifying the testing procedure; in fact the only precautions which need be taken are:

(1) Elimination of the calender effect in the rubber mixture by repeated calendering in cross-directions.

(2) Good condition of the die for cutting out the ring specimens.

As far as comparative tests with dumb-bell and ring test-specimens are concerned, a few results of a direct comparison between dumb-bell and ring test-specimens, carried out by the procedure of the Socfin laboratory, are given in Figure 4.

The graphs in Figure 4 show that the results are not comparable, either for modulus or for tensile strength; only the ultimate elongations are of the same order of magnitude.

It should be added that the apparatus used in these tests (a Schopper machine) was not equipped for testing dumb-bell specimens with 1-inch marks, as specified by the Crude Rubber Committee.

Insofar as simplicity and the possibility of reproducing results are concerned, ring specimens are clearly to be preferred to dumb-bell specimens.



## TESTING PROCEDURE WITH A MASTERBATCH

From the point of view of pure research, a testing procedure which utilizes a masterbatch is certainly to be condemned. The possibility of utilizing this method for the commercial or routine testing of plantation rubber should not be overlooked, for this method has the virtue of simplicity of testing technique.

For example, for testing ten batches, each of 200 grams of rubber from different sources, three steps are sufficient:

- (1) To prepare beforehand a masterbatch of the following composition:

	Grams
Rubber .....	200
Sulfur .....	77
Stearic acid .....	11
Mercaptobenzothiazole .....	11
Zinc oxide .....	132
Total .....	431

- (2) To divide this masterbatch into 10 equal parts of 43.1 grams each.

- (3) To mix each aliquot portion of the masterbatch with the particular rubber samples to be tested. The total weight of each mixture is then 243.1 grams, of which 220 grams is rubber, i. e., 200 grams of rubber to be tested and 20 grams of rubber contained in the masterbatch (10 per cent of the total rubber).

The greater accuracy with which the ingredients can be weighed because of the larger quantities involved, and the ease with which the masterbatch can be mixed with the rubber to be tested, are factors which favor of this method.

The effect of the rubber used for preparing the masterbatch on the sample of rubber to be tested was therefore studied. Three conditions were investigated:

- (1) Using rubber which vulcanized slowly and rubber which vulcanized rapidly.

- (2) Using masterbatches prepared from each of these rubbers.

- (3) Testing each of these rubbers, with and without the use of a masterbatch.

The results obtained are summarized in Table III.

TABLE III

Type of rubber tested	Masterbatch		Modulus		Tensile strength
	Addition	Rubber used as a base	550%	700%	
Slowly vulcanizing	No	.....	18	39.5	96
	Yes	Slowly vulcanizing ....	15.5	34	91
	Yes	Rapidly vulcanizing ...	17.5	38.5	100
Rapidly vulcanizing	No	.....	25	63	138
	Yes	Slowly vulcanizing ....	21	50.5	127
	Yes	Rapidly vulcanizing ...	22	52	130

These results show first of all that, whether or not the rubber under investigation vulcanizes slowly or rapidly, better quality is obtained without the use of a masterbatch, that the masterbatch plays an unfortunately important part in the results, and consequently that the method is not suitable for general use.

The tests described above were carried out with batches weighing 200 grams, and the addition of 10 per cent of rubber in the form of a masterbatch had considerable influence on the resulting quality.

## SUMMARY

To simplify the testing procedure and to make it possible to reproduce results in different laboratories more easily, it is recommended:

(1) That laboratories adopt ring test-specimens instead of dumb-bell specimens.

(2) That the use of a masterbatch in preparing batches be avoided, in spite of the advantage which it offers in simplicity of technique.

## COMPLEMENTARY SPECIFICATIONS NECESSARY TO MAKE THE TESTING PROCEDURE MORE PRECISE

The lack of precision in certain parts of the specifications of the Crude Rubber Committee arises chiefly from the fact that the authors have purposely left open the choice of what weight of batch to use. Under these conditions, it was almost impossible to specify the times and exact operating technique to be followed.

By recommending a maximum weight of batch of 200 grams of rubber, plus ingredients, for testing rubber commercially, it becomes possible to make the present specifications more precise in certain ways, both with respect to the preparation of the rubber mixes, and with respect to the vulcanization of these mixes.

## PREPARATION OF THE MIXES

The technique of preparing the rubber mixes can be divided into four parts:

(1) Plasticization of the raw rubber.

(2) Addition of the compounding ingredients and their incorporation into the rubber.

(3) Blending of the mixture.

(4) Calendering of the mixed batch.

In the following paragraphs, these four periods will be discussed, assuming throughout the discussion a test-batch with a volume between 200 and 250 cc.

*Plasticization.*—The results of tests, shown in Figure 5, prove that the tensile strength varies markedly with increase in the time of plasticization. It is necessary therefore to specify a definite time of plasticization, and it is suggested that, for batches of 200-250 cc., this time be fixed at 2 minutes (with the rolls at 65° C and spaced 0.35 mm. apart). This period of 2 minutes is sufficient to plasticize the rubber satisfactorily.

*Addition and Incorporation of Compounding Ingredients.*—This procedure is described in the specifications of the Crude Rubber Committee, and can be carried out in 3 minutes with a batch of 200-250 cc., and the mill rolls at 65° C and 0.35 mm. apart. It is recommended that this period of 3 minutes be adopted.

*Blending of the Batch.*—Here too the procedure specified by the Crude Rubber Committee is quite satisfactory, with six passes in 3.5 minutes for a batch of 200-250 cc., and with the mill rolls at 65° C and 0.35 mm. apart.

*Calendering.*—The procedure described by the Crude Rubber Committee was designed for tests with dumb-bell specimens and, in our opinion, has the fault of giving to the rubber a calender grain. Exactly the same modulus values and slightly higher tensile strengths have been obtained in the Socfin laboratories by calendering in the following way:

(1) The mill rolls are spaced 0.70 mm. apart and are heated to 65° C.

(2) The mixed batch is passed 4 times through the rolls.

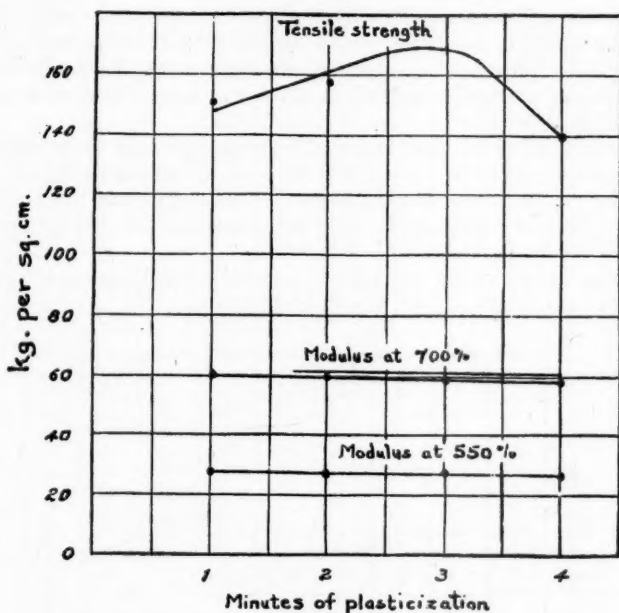


FIG. 5.—Influence of the time of plasticization during the mixing operation.

(3) After each pass through the mill, the rubber is rolled up and inserted into the mill again by the end of the rolled-up piece.

This operation requires 1.5 minutes.

*Specifications for the Mixing Operation.*—It is proposed that the scheme shown in Table IV be followed for a sample of 200 grams of rubber to be tested:

TABLE IV

Operation	Time (min.)	Spacing of the mill rolls (mm.)	Procedure
Plasticization .....	2	0.35	Crude Rubber Committee specifications.
Mixing .....	3	0.35	Crude Rubber Committee specifications.
Blending .....	3.5	none	Crude Rubber Committee specifications.
Calendering .....	1.5	0.70	Four passes in alternating directions.
Total .....	10.0	—	Rolls at 65° C.

*Vulcanization.*—The state of vulcanization of a rubber mixture is normally dependent on the temperature and the time of vulcanization. In a steam autoclave, with the moulds so arranged that there is free circulation of steam, it is reasonable to assume that a thermometer in a receptacle filled with oil and inserted 10 cm. into the interior of the autoclave will give the temperature of vulcanization within 1° C.

Equipment for controlling the inflow of steam as a function of the variation of temperature can be installed on the autoclave, so that the temperature can be controlled automatically.

With respect to measuring the time of vulcanization, the specifications of the Crude Rubber Committee are not very explicit; in fact, according to these specifications, the time of vulcanization is understood to be from the moment when the ram of the press reaches its maximum height to the moment when the pressure is released.

Obviously this definition does not apply to an autoclave. For the latter, the definition must be reworded, *i. e.*, the time of vulcanization in an autoclave can be defined as the time elapsed from the moment when the specified temperature of vulcanization is reached to the moment when the steam supply is shut off and the discharge valve is opened.

This method of measuring the time of vulcanization is the one which is employed in the laboratory of the Socfin Company.

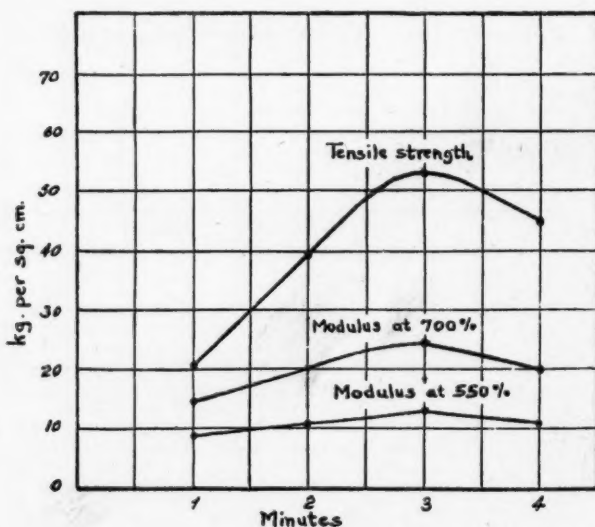


FIG. 6.—Influence of the time of admission of steam into the autoclave.

However, such a specification for measuring the time of vulcanization is inadequate; for it is also necessary to define:

(1) The time required to reach the vulcanizing temperature in the autoclave.

(2) The time required to discharge the steam from the autoclave, to remove the moulds, and to cool the samples.

The time required for (1) depends on the volume of the autoclave, on the dimensions of the inlet steam line, and on the steam pressure. Figure 6 shows the results of tests carried out to determine the part played by this initial period. It is evident from these graphs that the time required to reach the desired steam pressure has an important influence on the results. It is necessary therefore to prescribe the time for the moulds to reach the temperature specified. In the Socfin laboratory this time is fixed at 2 minutes.

The time required to discharge the steam, to remove the moulds and to cool the samples depends on the volume of the autoclave, on the dimensions of the discharge steam line and on the means of opening the doors of the autoclave.

Figure 7 shows that this final period in the vulcanizing operations is far from negligible, especially when the time of vulcanization is short. In the Socfin laboratory this final period has been fixed at 3 minutes.

*Specification for Measuring the Time of Vulcanization.*—From the results of the tests and from what has been said, it is evident that the total time of vulcanization can be divided into several periods, and that it is absolutely necessary to specify definitely:

- (1) The time of vulcanization in the autoclave.
- (2) The time necessary to reach the temperature of vulcanization, *e. g.*, 2 minutes.
- (3) The time necessary to begin cooling the moulds with water after vulcanization is complete, *e. g.*, 3 minutes.

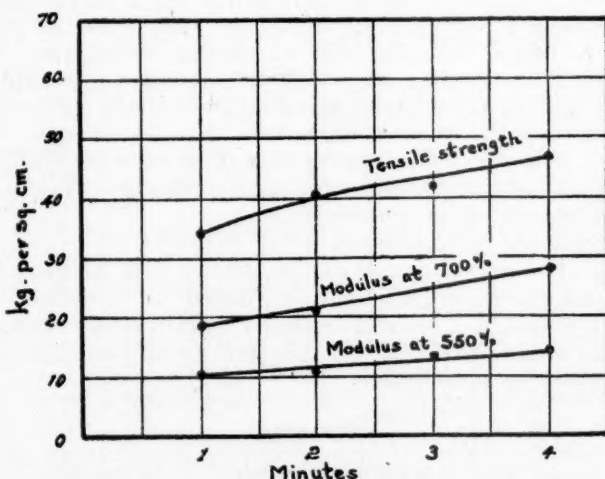


FIG. 7.—Influence of the time of discharge of steam from the autoclave.

The time of vulcanization, properly speaking, can be measured either:

- (1) From the moment that the autoclave is closed and the steam is turned on (period (1) + (2)), or
- (2) From the moment when the temperature of vulcanization is reached (period (2) only).

In testing rubber at the Socfin laboratory, the method adopted has, as mentioned above, been to measure the time from the moment that the vulcanizing temperature is reached.

#### SUPPLEMENTARY REMARKS

In April 1936 the Crude Rubber Committee of the Division of Rubber Chemistry of the American Chemical Society recommended:

- (1) That a mercaptobenzothiazole (Captax) formula be adopted for determining the variability of rubber.
- (2) That the rubber be tested according to the specifications of the American Society of Testing Materials, which were reviewed in this study.



(3) A vulcanizing temperature of 260° F (126.7° C) be adopted, and that cures of 20, 30, 40, 60 and 80 minutes be made, with the stipulation however that in control testing, a single cure of 40 minutes may be satisfactory for some purposes.

It is quite evident that in the commercial testing of plantation rubber for sale on a basis of quality, it will be preferable to prescribe a single temperature and also a single time of vulcanization. The great number of tests which would otherwise have to be made and the expense of making them justify this method.

We believe that the choice of 40 minutes as the time of cure is a desirable one. On the contrary, tests in the Socfin laboratory, as well as tests by other laboratories in the Far East, show that a vulcanizing temperature of 126.7° C is unsatisfactory.

To substantiate this latter statement, tests recorded in Figures 8 and 9 show that rubber samples were distinctly undercured when vulcanized at 126.7° C, even when the time of vulcanization was more than 100 minutes. These same graphs show that the optimum temperature of vulcanization was approximately 280° F (138° C). At this temperature and after 40 minutes' vulcanization, the rubber samples were still slightly undercured.

As a result of these tests, it would appear to be advisable, with the testing procedure which we have recommended, to prescribe the following conditions for testing plantation rubber commercially:

(1) A temperature of vulcanization of 280° F (138° C).

(2) A time of vulcanization of 40 minutes, counted from the moment when the vulcanizing temperature of 280° F has been reached in the autoclave.

On the other hand, if it seems desirable for other reasons to continue to use a temperature of 260° F (126.7° C), then the time of vulcanization should be fixed at 60 minutes as a minimum.

#### SUMMARY

The investigation which has just been described can be summarized as follows:

(1) A technique for the commercial testing of plantation rubber has been developed which is simple and precise, and by means of which it is possible to reproduce control tests, a feature which is indispensable if rubber is to be sold on a basis of quality rather than superficial appearance.

(2) The tentative specifications for testing rubber drawn up by the Crude Rubber Committee of the Division of Rubber Chemistry of the American Chemical Society have been found acceptable as a basis for this testing procedure.

(3) It has been found necessary, however, to revise the specifications of the Crude Rubber Committee in some ways and to amplify them, so that they fulfill the three conditions described above and also conform to the particular working conditions of laboratories in the tropics.

The revisions to the Crude Rubber Committee specifications include:

(1) The use of an autoclave for vulcanizing in open steam.

(2) A mill roll temperature of 65° C instead of 70° C.

(3) A definite, fixed weight of batch, containing 200 grams of rubber, plus accessory ingredients.

(4) A temperature of 25° to 30° C during testing.

(5) The use of ring test-specimens instead of dumb-bell specimens.

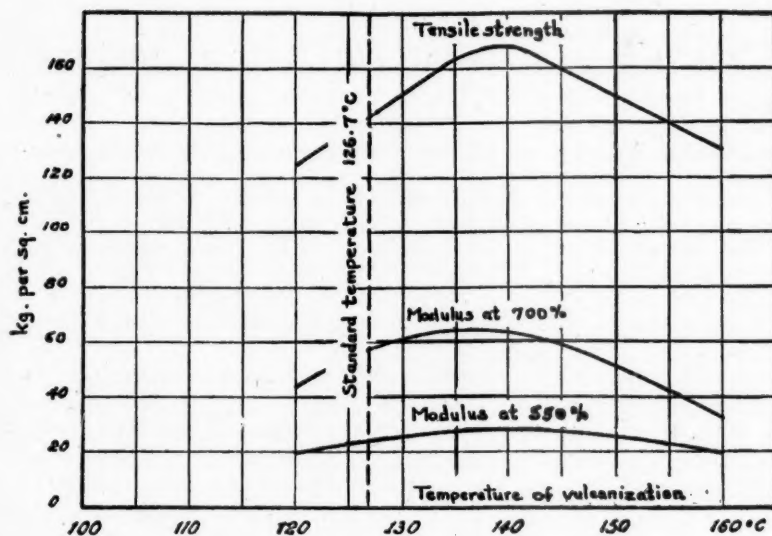


FIG. 8.—Influence of the temperature of vulcanization.

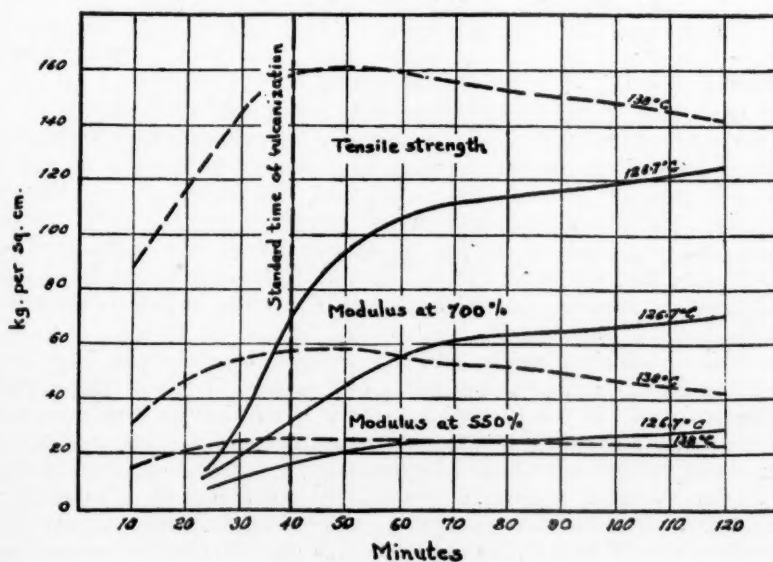


FIG. 9.—Influence of the time of vulcanization.

The specifications to be defined in precise terms are as follows:

- (1) The times of the mixing operations.
- (2) The time of vulcanization in open steam, particularly the time of rise to the vulcanizing temperature and the time of cooling.
- (3) The temperature and time of vulcanization which are most suitable for classifying rubbers, viz., 138° C for 40 minutes or 126.7° C for 60 minutes.

# THE PROBLEM OF CRUDE RUBBER \*

A. THOMAS

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In recent years, rubber manufacturers have made tremendous progress in compounding and in methods of manufacture, yet they continue, as they always have done, to regard smoked sheet and crepe from the plantations as the essential raw material of their industry. As a matter of fact, however, latex is the essential raw material, and the changes which it undergoes on the plantations are among the factors which influence the quality of the final rubber and therefore play a part in its possible uses.

In the face of this, it seems like a paradox to say that the processing of latex on the plantations is based on arbitrary methods, without any consideration taken of their effects on the properties of the finished rubber, whereas mixing and vulcanizing operations are scrupulously controlled by manufacturers.

For what reason does this paradoxical situation continue to prevail? Only because of the way by which the broker still evaluates rubber. The plantations are obliged to classify their commercial product into different types, according to color, superficial appearance, cleanness and the presence or absence of bubbles in sheet rubber, with complete disregard to its intrinsic properties, the latter not even being measured. To be regarded as the best quality, commercial rubber must be of a uniform color, must have a regular surface and must contain neither impurities nor bubbles.

Let us consider what unscientific methods the planter must employ to obtain the maximum production of rubber of the first quality. As it comes from the trees, latex differs greatly according to its age, its origin and the soil on which the trees are planted. Because of this, the specific gravity, chemical composition, stability and pH values vary, and they are more or less subject to biological and chemical changes by microorganisms and enzymes. These latter changes, generally designated as maturation phenomena, may bring about spontaneous coagulation, and the formation of bubbles in sheet rubber may generally be attributed to them.

To avoid bubbles, the rubber grower first treats his latex with large doses of anticoagulants, usually sodium sulfide or ammonia. Whereas, for example, 0.5 gram of ammonia per kilogram of rubber is sufficient to keep even latex with the greatest tendency to coagulate prematurely in a stable condition, it is not unusual to find as much as 1.5 grams or even 2 grams being used to paralyze all bacteriological action and to avoid bubbles caused by precoagulation.

With the same end in view, the rubber grower is led to dilute his latex before coagulation, to use tremendous doses of acid and, further to paralyze any changes which might occur in the coagulum, to heat the coagulum from the beginning at relatively high temperatures, and to utilize the antiseptic properties of smoke.

What are the results of this process? The resulting sheet rubber certainly has an attractive appearance, it is clear and transparent, it is uniformly smoked and it has no visible faults; yet if two sheets chosen at random from the same

\* Extracted from a paper by the same title in *Le Caoutchouc et la Gutta-percha*, Vol. 36, No. 425, 171-172; No. 426, 199-200 (1939).

day's production are tested, it will be found that their tensile strengths, rates of vulcanization, plasticities and resistances to aging may differ as much as 100 per cent. This is the major fault to which the manufacturers object, viz., that plantation rubber is not of uniform quality, and that this variability is a source of constant trouble, making it necessary to carry out long and burdensome blending operations and still not be able to maintain uniformity in manufacture.

If, on the contrary, we disregard the appearance of sheet rubber, and instead undertake a systematic study of latex and the changes which take place in it, it will be evident not only that present methods of production do not guarantee a uniform product but also that they lower some of the inherent good properties of the rubber.

In support of this statement, there are tabulated below the results of analyses of ten samples taken from a shipment of rubber of the highest commercial quality (1-X ribbed smoked sheet) and eleven samples taken from a lot of rubber which had been produced without regard to superficial appearance but, instead, with the aim of preparing a uniform product of high tensile strength and fast rate of vulcanization.

Recipe used:

Rubber .....	200
Sulfur .....	7
Mercaptobenzothiazole (Captax) ....	1
Stearic acid .....	1
Zinc oxide .....	12

Temperature of vulcanization.....126.7° C  
Time of vulcanization.....40 minutes

#### TENSILE TESTS

		Stress (in kg. per sq. cm.)				Elongation at rupture (percentage)
		500% elongation	600% elongation	700% elongation	At rupture	
Ordinary commercial rubber.	1	16	25.5	44.5	137.5	912
	2	14	22	39	120	912
	3	19	30	53	127	872
	4	19	33	57.5	128	852
	5	18	30	54	148	892
	6	14	21	36	99	887
	7	13.5	20	33	115	932
	8	18	29	52	140	885
	9	15	32	57	107	890
	10	15.5	23.5	40	127	912
Uniform rubber of high strength and fast rate of vulcanization.	2277	29	52	97.5	203	839
	2278	31	56	105	195	812.5
	2279	31	57	106	201	819
	2280	30	54	102	174	799
	2281	28.5	51	97	198.5	836
	2282	28.5	52	98	195	832
	2283	30	55	102.5	193	813
	2284	28	49.5	91.5	189	839
	2300	29	53	99.5	183	832
	2301	30	54	100	185	819
	2302	29	52	98	211	835

## CHEMICAL ANALYSES (IN PERCENTAGE)

		Moisture	Water soluble	Resins	Protein	Ash
Ordinary commercial rubber.	1	0.95	1.64	2.70	2.756	0.30
	2	0.80	0.802	3.06	2.756	0.30
	3	0.85	0.702	2.94	2.853	0.35
	4	1.00	1.04	2.88	2.712	0.35
	5	0.75	0.52	3.10	2.887	0.32
	6	1.00	1.02	3.02	2.668	0.45
	7	1.00	1.32	2.74	2.668	0.45
	8	0.85	1.12	2.74	3.281	0.30
	9	0.90	1.72	2.74	2.853	0.40
	10	1.00	1.14	3.04	2.887	0.37
Uniform rubber of high strength and fast rate of vulcanization.	2277	1.20	1.30	2.70	2.800	0.47
	2278	1.25	1.10	2.40	2.800	0.48
	2279	1.00	1.10	2.80	2.712	0.46
	2280	1.25	1.50	2.50	2.800	0.49
	2281	1.00	1.10	2.70	2.625	0.50
	2282	1.00	1.10	2.70	2.712	0.45
	2283	1.00	1.70	2.40	2.625	0.49
	2284	1.00	1.30	2.40	2.625	0.48
	2300	1.00	1.00	2.50	2.887	0.47
	2301	1.05	1.00	2.50	2.975	0.48
	2302	1.25	1.20	2.50	2.887	0.50

These tabulated results show the possibilities of which advantage may be taken, but in no way do they offer a solution of the problem. The optimum properties may differ according to the ultimate use to which the rubber will be put, and unquestionably rubber producers can vary these properties to meet the requirements of the purchaser. To attain this result, it is necessary:

(1) to establish methods of analysis and standard testing methods analogous to those for other ordinary raw materials;

(2) to abandon the ridiculous classification now in use, and to replace it by a rational classification based on the tests mentioned above. Each branch of the rubber industry can then have its own specifications, and the rubber producers will be in a position to specialize in definite types of rubber, *e. g.*, rubber best suited for automobile tires, for electric cables, for oil-resistant products, for water-resistant products, for very soft products, for different types of latex, etc.

Unfortunately the manufacturers are inclined to conceal their own methods, to regard the problem of uniformity as within the domain of the rubber producers, to consider improvements as a problem of their own, and to feel that competition is an obstacle to collaboration.

At the present time there are various special rubbers, including softened rubber, deproteinized rubber, powdered rubber, sprayed rubber, concentrated latex, creamed latex, centrifuged latex, etc., which are produced without much more technical skill than that in the production of smoked sheet and crepes. These special types of rubber fulfill in an uncertain way the requirements of certain industries. If it were possible to have precise control over production on the plantations, these special rubbers would increase, new uses would become possible, and it might be possible to compete effectively with the various synthetic products which may at any time become a serious threat to culture of *Hevea* rubber.

Today modern plantations have equipment of the best kind, and if this equipment is to be supplemented by laboratory equipment for controlling produc-



tion, it will be necessary for technologists to adapt themselves to the new methods; and to prepare for the future the plantations must have rubber technologists such as those now in the rubber manufacturing industry. The importance of rubber in modern industry justifies the establishment of special technical training, and it would be particularly desirable if the study of rubber were to be included in the courses of important schools. Natural rubber is a new product, is still little understood, and offers an inexhaustible field of investigation. If research on rubber is conducted systematically, and if sufficient support is assured to the organizations which are to carry on these investigations, important discoveries will certainly be made, and these will in turn increase to a considerable extent the industrial applications of natural rubber.

[In another article, published in *la Revue Générale du Caoutchouc*, Vol. 16, No. 7 (September 1939) and No. 8 (October 1939), the same author discusses in all its phases the culture of *Hevea* rubber in Indochina. In the preceding work, three proposals were offered as means of improving the quality of sheet rubber:

(1) that it is necessary to abandon the present method of grading rubber in favor of a specification as precise as are the specifications for other important raw materials;

(2) that this specification be such that the production of rubber can be controlled and the uniformity required by rubber manufacturers be attained;

(3) that the manufacturers specify the properties desired, and that attempts then be made to improve rubber to meet these requirements.

It is pointed out by the author that the second and third of these proposals are so closely related that they can hardly be treated separately.]

When a study of the causes of the variability of commercial rubber is undertaken, it is found that the properties of the latex have a surprising influence in the case of certain types of rubber mixtures.

It has been believed, on the basis of experiences with rubber-sulfur mixtures, that variations in quality due to the quality of the original latex rarely exceed 10 per cent, whereas variations in manufacture are around 90 per cent. Perfect control of manufacturing processes is therefore all that is necessary to obtain uniform rubber products. However, the problem is not so simple as this.

We have studied the variability which is attributable to latex in the case of rubber mixtures accelerated by mercaptobenzothiazole. With this accelerator at least, variations due to differences in the latex are large. The following table, for example, gives the properties of rubber, prepared under identical conditions but from latices of different character, vulcanized at the same time in the same mixture. The data in the table give an idea of the variability which may be found. It is evident that the quality of rubber varies with the age of the tree, and that in any future study it will be necessary to include a study of seasonal variations.

#### MIXTURE

Rubber .....	200
Sulfur .....	7
Stearic acid .....	1
Mercaptobenzothiazole (Captax) ....	1
Zinc oxide .....	12
Vulcanization .....	40 min. at 126.7° C

Age of culture	TENSILE TESTS				Elongation at rupture (percentage)
	Stress (kg. per sq. cm.)				
	500% elongation	600% elongation	700% elongation	At rupture	
1916	12.5	18.5	31.5	104	947
1917	13	21.5	37.5	115	928
1923	17	26.5	45.5	121	910
1926	19.5	32	57	122	855
1931	21.5	36	64	149.5	878

Experiments should be made to ascertain whether variations of the same order of magnitude occur with other accelerators, *e. g.*, with diphenylguanidine. If such turns out to be the case, the influence of latex will alter the problem completely, and may even change the point of view of the manufacturer. As a matter of fact, it is difficult to prepare mixtures of latex sufficiently uniform to make it practical to adopt a single method of production of rubber, and it is going to be necessary to vary some step, perhaps several steps, in producing crude rubber, to counterbalance the influence of the latex and thus to arrive at a uniform final product. It will be necessary to choose a standard of quality which is inferior to that which would be possible if no regard were taken of uniformity and if each lot of latex were treated under optimum conditions, the task of making the rubber uniform being left to the manufacturer, who would then blend rubbers of high but differing quality to obtain the best product possible.

Does the manufacturer value uniformity above all other properties, and does he prefer rubber of relatively poor quality, provided only that it is uniform? This is one of the many problems which can be settled only by close collaboration between producer and manufacturer.

We have studied the influence of all the factors involved in collecting latex, and in processing it, on the tensile strength and the rate of vulcanization of the resulting rubber, using the accelerated mixture of the Crude Rubber Committee of the Division of Rubber Chemistry of the American Chemical Society. The tests are being continued with a study of the influence of these factors on the aging, plasticity, viscosity and chemical composition of crude rubber. Experiments of a similar kind will be made with other rubber mixtures, *e. g.*, with the use of diphenylguanidine instead of mercaptobenzothiazole (Captax) as accelerator.

In this way it has been possible to determine the method of production which gives, in the present state of our knowledge, rubber of the highest tensile strength or rubber with the fastest rate of vulcanization.

As representative of the results obtained, data on tests of rubber produced under the conditions now prevailing on the plantations, and tests of a type of rubber produced from the same latex but by methods which yield a product with the maximum tensile strength, are given in the table on opposite page.

We do not say positively that the fast-curing rubber is superior to the other rubber, for the manufacturer must decide to what extent he is interested in a type of rubber which vulcanizes rapidly and has a high tensile strength. Nevertheless, we believe that, if its other properties, such as aging, resistance to abrasion, resistance to flexing, resistance to tearing, etc., are likewise superior, then fast-curing rubber is the superior type. But whatever is the answer, the tests show the possibilities, and they prove convincingly that the objections to ordinary rubber arise solely from the fact that no means are available at present for controlling production.

If the manufacturers will agree among themselves, and then with the rubber producers, on a complete method of testing, and if the manufacturers will then specify the properties desired, it will certainly be possible to control the production of rubber so as to obtain the type of rubber requested.

American manufacturers do not seem to be very much interested in rubber with a fast rate of vulcanization. They profess to be unable to control the effects of active natural accelerators, whether these function as true accelerators or as activators of chemical accelerators added to the rubber mixtures. On the contrary, some European manufacturers seem to be interested in rubber which contains the highest possible amount of natural accelerators. Probably this divergence of views arises, at least in part, from the fact that the accelerators

## FIRST MIXTURE USED

Rubber .....	200
Sulfur .....	7
Stearic acid .....	1
Mercaptobenzothiazole .....	1
Zinc oxide .....	12

Vulcanization .....40 minutes at 126.7° C

Type of rubber	Stress (kg. per sq. cm.)				Elongation at rupture (percentage)
	500% elongation	600% elongation	700% elongation	At rupture	
Ordinary .....	19	31.5	56.5	153	979
Fast-curing .....	34.5	65	124	227	819

## SECOND MIXTURE USED

Rubber .....	200
Sulfur .....	5.5
Diphenylguanidine .....	0.8
Zinc oxide .....	12

Vulcanization .....40 minutes at 141° C

Type of rubber	Stress (kg. per sq. cm.)				Elongation at rupture (percentage)
	500% elongation	600% elongation	700% elongation	At rupture	
Ordinary .....	8.5	11.3	16.75	71.5	1019
Fast-curing .....	16.75	27.75	50	153	912

used in rubber in Europe are not the same as those used in America. It is, for example, possible that the natural accelerators present in latex act differently, according to whether mercaptobenzothiazole or diphenylguanidine is present in the rubber.

In general, then, there are sure to be numerous difficulties encountered in improving the quality of rubber; mistakes will be made, and there will be disagreements, for it is a question of replacing an established system by something new, and it may in some cases be difficult to estimate the advantages to be gained by those concerned, *i. e.*, the rubber growers, the brokers, and the manufacturers. Isolated efforts have no chance of success, and it is by the concerted action of many in quickly establishing the necessary connections, and in breaking down the barriers which now separate the manufacturers from the rubber growers, that there will be any likelihood of settling the problem.

# THE VISCOSITY OF PRESERVED AND CONCENTRATED LATEX

## PART I. RELATIONSHIP BETWEEN DRY RUBBER CONTENT AND VISCOSITY

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In the October 1939 issue of RUBBER CHEMISTRY AND TECHNOLOGY, on pages 655-664, is an article of the above title by Edgar Rhodes. Since the time of its original publication in the *India-Rubber Journal*, in January 1939, the work has been revised and published in the *Journal of the Rubber Research Institute of Malaya*, Vol. 9, pages 171-188 (Communication no. 241), December 1939. The attention of RUBBER CHEMISTRY AND TECHNOLOGY has been called by Mr. H. J. Page, Director of The Rubber Research Institute of Malaya, to the importance of certain revisions in Part I of the work. Mr. Page points out, for example, that "the authors have evaluated separate relationships for ammoniated field latex and for centrifugal concentrates, thereby revising the estimates of the average viscosity of latex of varying dry rubber content at 30° C." These new data are given in Tables I and II.

The discussion on pages 657 and 661-663 of the same issue of RUBBER CHEMISTRY AND TECHNOLOGY has been altered considerably, and therefore is reproduced in full here.

### DISCUSSION

When tested at low rates of shear, latex, like other colloidal suspensions, may show varying coefficients of viscosity, depending on the rate at which it is measured<sup>1</sup>. In the following discussion we assumed that our observations represent "limiting coefficients of viscosity". We make this assumption because results obtained with two different viscometers are very similar, and because there is no discontinuity at points where observations with the Höppler viscometer have been made with balls of different weights.

Since the main purpose of this work is merely to obtain descriptive data, no attempt has been made to investigate the theory of the subject. But in seeking an empirical formula by which the data may be conveniently described, we have taken the opportunity to compare our observations with some of the equations which have been put forward.

Most theoretical work on the viscosity of suspensions starts from the work of Einstein<sup>2</sup>. For very dilute suspensions of rigid spherical particles in a dispersion medium of equal density, he derived theoretically, from hydrodynamic considerations, the relationship:

$$\eta = \eta_0(1 + 2.5\phi) \quad (1)$$

where  $\phi$  is the volume of the disperse phase in unit volumes of the dispersion,  $\eta$  is the viscosity of dispersion, and  $\eta_0$  is the viscosity of the dispersion medium.

Assuming that the relative specific gravity of the rubber phase is 0.910 and of serum is 1.022 (H. F. Smith, 1939), and that the volume of the disperse phase

is not increased over the volume of rubber by water of hydration and other adsorbed substances, we may put as estimates of  $\phi$  in our data:

$$\phi = \frac{1.022w}{0.910 + 0.112w} \quad (2)$$

where  $w$  is the weight of rubber in unit weight of latex.

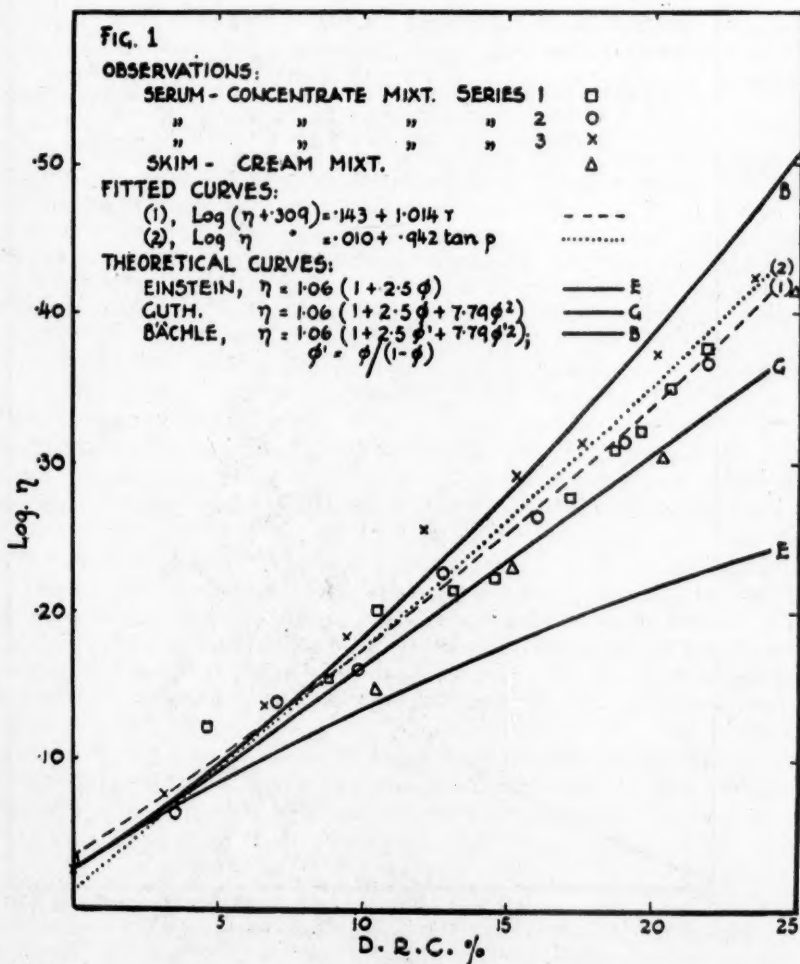


FIG. 1.

Figure 1 shows that the rate of change of viscosity with concentration in dilute suspensions of latex-serum mixtures is perhaps slightly greater than, yet not dissimilar to, that predicted by Einstein's law. Our data are not suitable to determine this point accurately, since there are no observations on suspensions with less than 3 per cent d.r.c.; but for Equations (1) and (2), which have been fitted to the data for serum-concentrate mixtures, the values of



$\frac{d(\eta/\eta_0)}{d\phi}$ , when  $\phi=0$ , are 2.68 and 3.37, respectively; Einstein's law predicts 2.5.

Guth and his coworkers have considered adjustments to Einstein's law for forces of inertia, influence of viscometer wall, mutual action of the suspended

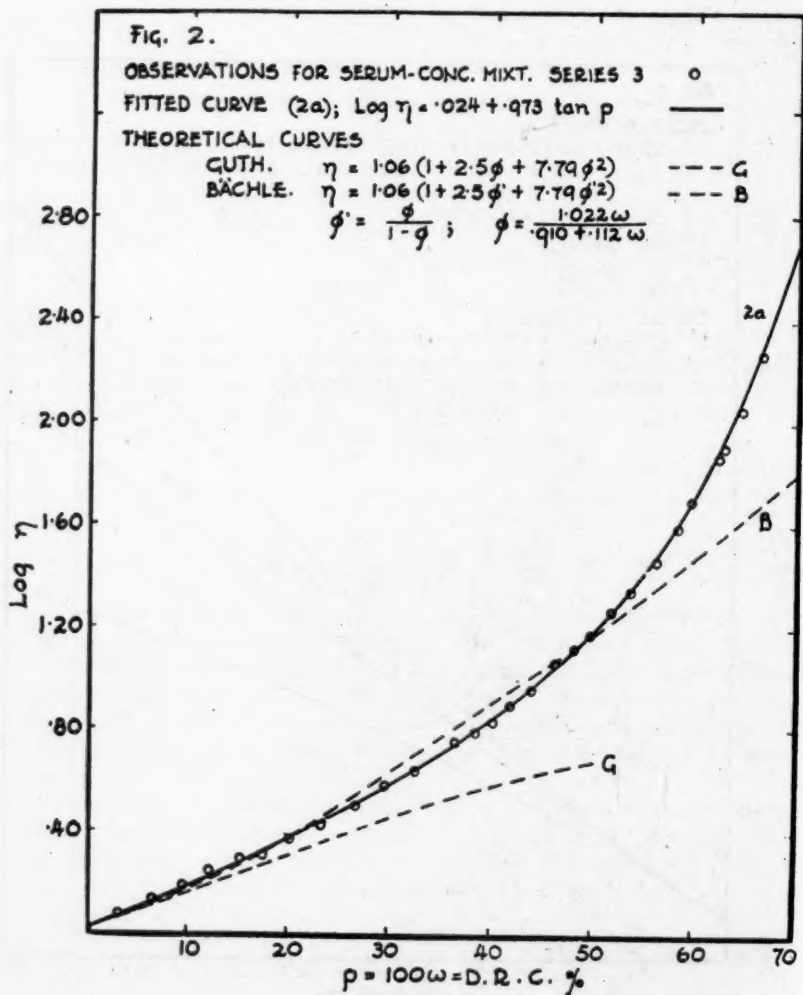


FIG. 2.

particles on each other, electro-viscosity and Brownian motion. Of these, adjustment for interaction of the particles becomes most important with increasing concentration; it is the only one which will be considered here. Guth<sup>4</sup> evaluated this adjustment as an expansion in powers of  $\phi$ , for which he has so far obtained only the coefficient for the quadratic term, viz.:

$$\phi = \eta_0 (1 + 2.5\phi + 7.79\phi^2 + \dots)$$

This equation is of interest in that, having all the constants (except  $\eta_0$ ) theoretically determined independently of any observations, it does succeed in forecasting observations fairly well between 3 and 15 per cent d.r.c. (Figure 1). Above this it may be supposed that the missing terms with higher powers of  $\phi$  become important. It would be of theoretical interest to investigate more thoroughly conditions in the region of 0 to 3 per cent d.r.c.

Bächle<sup>5</sup> compared his observations on latex with Guth's equation; but instead of  $\phi$  he used  $\phi/(1-\phi)$ , i. e., the ratio of disperse phase: serum<sup>6</sup>. With this modification he claimed that the equation gave a faultless (*tadellose*) agreement with his observations, up to 45 per cent d.r.c. The equation fits our data equally well (but not faultlessly), up to 50 per cent d.r.c.,  $\phi$  being estimated as above (see Figure 2)<sup>7</sup>.

Now Guth states that, when the corrections are larger than the basic value indicated by Einstein's equation, their construction by means of a power series is no longer permissible. In these circumstances he recommends that his equations should be used as giving no more than mere indications of the numerical values to be expected. He also suggested that they might be used as interpolation formulas, but since they are both complicated and inflexible, they seem to us to be inefficient for this purpose. Furthermore he considers that the superficial analogy to van der Waals' equation, by which some previous workers have replaced  $\phi$  in Einstein's equation by  $\phi/(1-\phi)$ , or  $\phi/(1-k\phi)$ <sup>8</sup>, is not permissible; and he apparently intends that the expansion in powers of  $\phi$  which he has proposed should replace this. Therefore when Bächle inserts  $\phi/(1-\phi)$  in Guth's equation, he would appear to be confusing ideas which were intended to be separate. Nevertheless the success of Bächle's equation suggests that it might deserve consideration by someone who is more competent than are we to investigate the theoretical background. Meantime, since independent justification appears at present to be lacking, it cannot be interpreted (as in Bächle's paper) "in support of the accuracy of measurements by the Höppler viscometer".

Whatever may be the theoretical interest of Bächle's equation, it is not suitable for use as a statistical tool to investigate variations which occur in practice: not only because it fails to describe observed viscosities over a sufficiently wide range; but also because, since it is inflexible in form, it cannot be fitted to different groups of data to estimate average values and to investigate differences between groups of latices.

For emulsoid sols in which the disperse phase consists of elastically deformable particles occupying more than one-half of the total volume, Hatschek<sup>9</sup> deduced a formula based on geometrical considerations, viz.:

$$\eta = \frac{\eta_0}{1 - \sqrt[3]{hw}}$$

where  $h$  is intended to be a hydration factor combined with the reciprocal of the specific gravity of the disperse phase, so that  $hw$  represents the volume of disperse phase, including water of hydration, in unit volume of the sol. He has applied this formula to estimate hypothetical values of  $h$  at varying concentrations. Applying this procedure to mean viscosities for the four mixture series we find:

$w$	0.02	0.30	0.37	0.52	0.56	0.66
$h$	0.011	1.09	1.34	1.58	1.58	1.48
$hw$	—	<.5	0.50	0.82	0.88	0.98

Since, with increasing concentration, the water of hydration, and therefore  $h$ , should either remain constant or decrease, it does not appear that this formula can have any meaning for latex of less than 52 per cent d.r.c.

Arrhenius<sup>10</sup> also has introduced the idea of hydration into his logarithmic formula, viz.:

$$\log \eta/\eta_0 = \frac{K w}{1 - (n+1) w}$$

where  $n$  is supposed to represent water of hydration. This formula fits the observations on latex very well, but since the regression of  $\log \eta$  on  $w(1-w)$  is concave downward (Figure 3),  $n$  must be negative. Therefore the formula can have no theoretical validity; and although it might serve very well as an empirical equation, more satisfactory ones can be devised.

In view of these comparisons of the viscosity of latex with the equations of Guth, Hatschek and Arrhenius, and of the close agreement of results obtained with two different viscometers, it might be tentatively suggested that latex seems to behave in these experiments as a hydrophobic sol. Obviously, however, no firm conclusion can be drawn on this evidence.

With no regard to theoretical considerations, a large number of formulas can be devised to describe the observations empirically. Of those which have occurred to us, we have selected two for detailed considerations, viz.:

$$\log (\eta + a) = b + cr \quad (\text{I})$$

$$\log (\eta) = a^1 + b^1 \tan p \quad (\text{II})$$

where  $r$  = ratio of rubber to serum =  $w/(1-w)$ ,  $w$  being, as above, weight concentration, or d.r.c. per cent  $\div 100$ ,  $p$  = d.r.c. per cent represented as an angle in degrees, and  $a$ ,  $b$  and  $c$  are arbitrary constants (of which  $a^1 = \log \eta_0$ ).

Equation (I) seems the more natural, since it has a fairly simple meaning. It indicates an approximately linear relationship between  $\log \eta$  and  $r$  when  $\eta$  is large relative to  $a$ , i. e., it indicates that relative changes in viscosity are approximately proportional to the ratio of rubber : serum. The constant  $a$  may be regarded as a correction factor for low concentrations. The equation is, for empirical purposes, similar to Arrhenius' equation, except that the adjustment for curvature of the regression of  $\log \eta$  on  $r$  has been introduced at a different place. It seems, however, to be preferable to Arrhenius' equation because, having abandoned the idea of hydration underlying Arrhenius' formula, Equation (I) is simpler in form and shows more clearly the interpretation just given. Furthermore, it seems to give a slightly truer description of the data. Arrhenius' equation fails to curve downward sufficiently near zero d.r.c., and is too low at the highest concentrations.

For statistical purposes, however, Equation (I) is not very convenient, since it gives  $\eta$  only as an implicit function of  $r$ , and cannot be readily fitted to any given set of data. Since, on the other hand, Equation (II) is a simple linear equation between two tabulated functions, it is ideal, both for statistical comparisons and as a simple formula to estimate viscosity of latex for any given d.r.c.

Both equations fit the data equally well. When they are fitted to the combined data of the four mixture series, and of the commercial samples (Höppler groups), allowance being made for differences between means of series but not for differences in slope, the mean variances of deviations of  $\log \eta$  from the regressions are:

	Mixtures	Commercial
From equation (I).....	$0.573 \times 10^{-3}$	$0.221 \times 10^{-3}$
From equation (II).....	$0.523 \times 10^{-3}$	$0.216 \times 10^{-3}$

The seven series of data have been compared by fitting Equation (II) to each separately. They show small differences both in slope ( $b^1$ ) and in the mean viscosities for any given d.r.c. Possible causes of these differences may be the source of latex, time of tapping, treatment of latex, or differences in the technique of testing, such as variation in the temperature between 28 and 30° C. The results will not, however, be set forth in detail, because from information now available it is not possible to disentangle the effects of these factors. As may be seen from the figures, the chief difference was that the serum-concentrate Series 1 and 2 and the skim-cream series (all from the same estate), and the Dunlop concentrate group, showed lower viscosities than Series 3 and the samples of field latex. The difference in  $\log \eta$  was of the order of .05, i. e., differences in absolute viscosity were about 12 per cent.

The best fitting regressions for the combined data of the four series of mixtures are (Figures 3 and 5):

$$\begin{aligned}\log(\eta+0.309) &= 0.143 + 1.014r & (1) \\ \log \eta &= 0.010 + 0.942 \tan p & (2)\end{aligned}$$

$\eta$  being measured in centipoises, and logarithms being to the base 10.

In estimating a mean regression for the samples of field latex, it must be borne in mind that the data are somewhat heterogeneous and, owing to the loss of the detailed data, we cannot now sort it out into groups representing different sources, times of tapping, etc. In particular it is known that the majority of the samples with low d.r.c. came from a division of one estate (Kepong), on which mild slaughter-tapping was being carried out. There is, therefore, reason to suppose that values of  $\eta$  below expectation in the lowest d.r.c. classes may be attributable to some special character of latex from this source, and may not represent the normal relationship between viscosity and d.r.c. in this region.

Now Equation (I) is sensitive to curvature in this region. If it is fitted to these data and extrapolated to  $r=0$ , it gives  $\eta_0=.83$ , which is too low, thereby tending to confirm our suspicion that the apparent curvature shown by the data for low values of d.r.c. may be an artifact. On the other hand, Equation (II) is not susceptible to this curvature. Therefore, for the purpose of estimating the average results for field latex, it seems preferable to use only Equation (II) and to ignore Equation (I).

Further, when pooling the data of Table I, it may be noted that the Höppler viscometer would be expected to give more accurate observations than could be obtained with the older and somewhat home-made pipette apparatus, which tended to show some irregularity at viscosities between 5 and 7 centipoises. Regressions fitted to each group separately showed variances about regressions of  $0.162 \times 10^{-3}$  and  $0.293 \times 10^{-3}$  for the Höppler and pipette groups, respectively. Therefore, to obtain an average regression for both groups, the pipette data have been weighted by 0.55 ( $=0.162/.293$ ).

The mean regression for the two groups is, (Figure 4):

$$\log \eta = 0.055 + 0.938 \tan p \quad (3)$$

The viscosities of the samples of centrifugal concentrates fall significantly below the values indicated by extrapolating Equation (3) (Figure 4). Furthermore the observations do not conform to a linear relationship of  $\log \eta$  or either  $r$  or  $\tan p$ . In fact the linear relationship appears to be between the primary variates,  $\eta$  and d.r.c., viz.:

$$\eta = -228.4 + 4.525 p \quad (4)$$





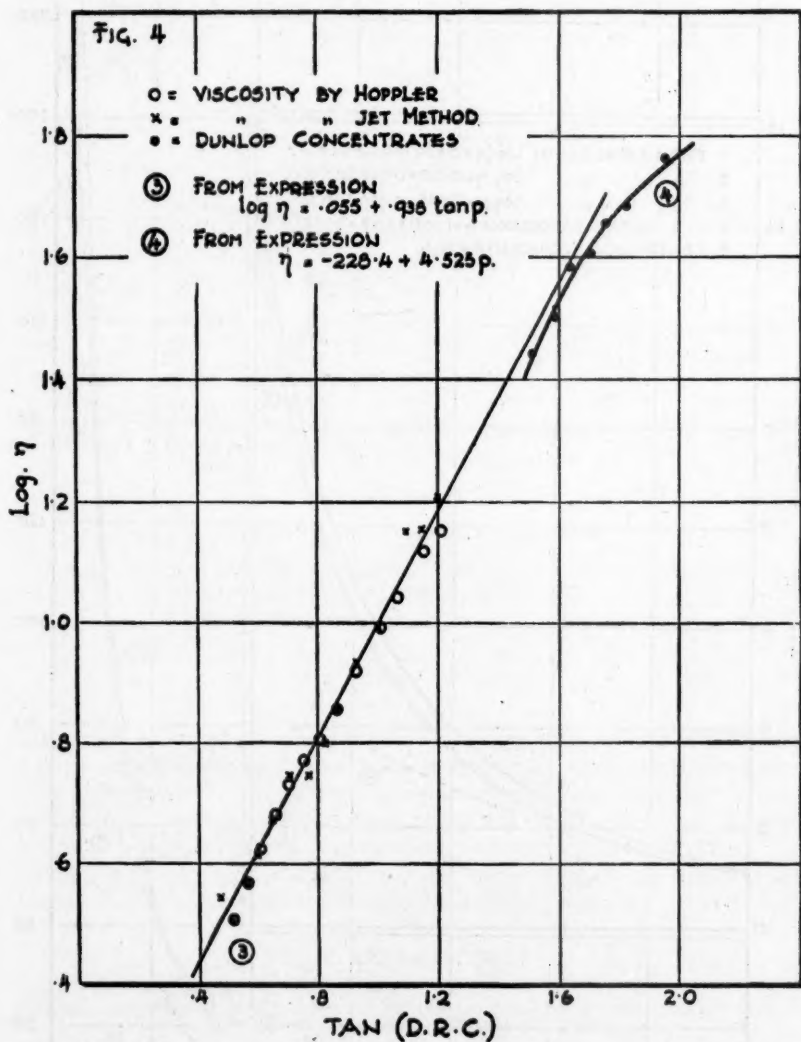


FIG. 4.

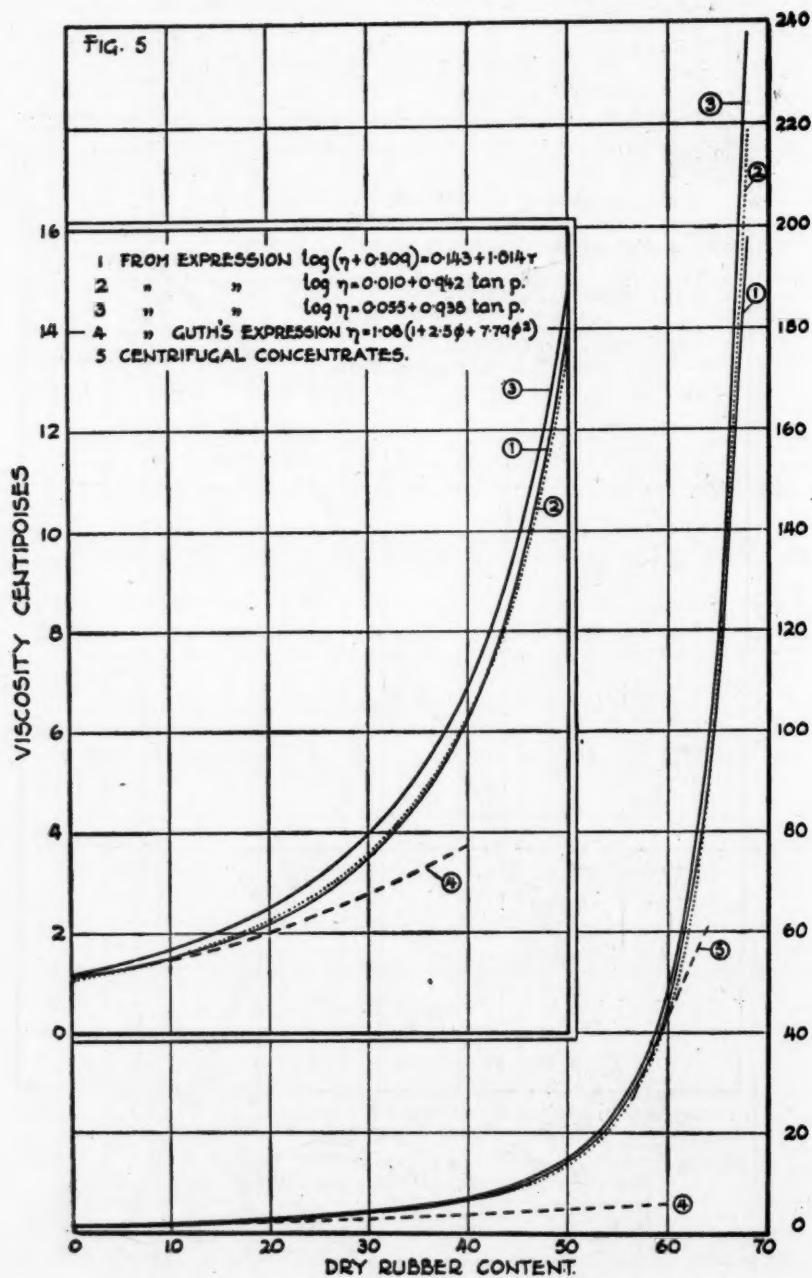


FIG. 5.

Obviously this relationship must be artificial, and cannot be extrapolated outside the observed range.

The general relationship between  $\eta$  and d.r.c. per cent is shown graphically in Figure 5, where Equations (1), (2), (3) and Guth's formula are compared<sup>11</sup>.

Tables I and II, based on Equations (3) and (4), may be used for reference to indicate the viscosity at 30° C of average ammoniated latex of any dry-rubber

TABLE I  
VISCOSITY OF LATEX AND LATEX CONCENTRATES  
(Viscosity at 30° C in centipoises)  
Ammoniated Field Latex

(Calculated from  $\log \eta = 0.055 + 0.938 \tan p$ , where  $\eta$  is the viscosity in centipoises, and  $p$  is the d.r.c. in percentage by weight).

Dry rubber content (percentage)	0	2	4	6	8
20.....	2.49	2.72	2.97	3.26	3.58
30.....	3.95	4.38	4.87	5.45	6.14
40.....	6.95	7.94	9.14	10.62	12.50
50.....	14.89	18.01	22.18	27.90	35.98
60.....	47.83	65.94	95.10	145.14	238.03

This table is to be read like a logarithm table, e. g., the viscosity of latex of 34 per cent dry rubber content = 4.87 centipoises.

TABLE II  
CENTRIFUGAL CONCENTRATES (DUNLOP)

(Calculated from  $\eta = 228.4 + 4.525 p$ , where  $\eta$  is the viscosity in centipoises, and  $p$  is the dry rubber content in percentage by weight).

Dry rubber content	56	58	60	62	64
$\eta$ .....	25.0	34.0	43.1	52.1	61.2

content. In so far as our samples may be representative of commercial samples at large, they indicate that individual samples may vary about the figures in Table I (field latex), with a standard deviation of 3.5 per cent (or 3.0 per cent for Höppler observations only), and about the figures in Table II (Dunlop centrifugal concentrates), with a standard deviation of 0.74 centipoise.

Tables I and II replace Table V in the earlier version, on page 664 of the October 1939 issue of RUBBER CHEMISTRY AND TECHNOLOGY.

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- <sup>1</sup> Madge, *Trans. Inst. Rubber Ind.* **10**, 398 (1935).
- <sup>2</sup> Einstein, *Ann. Physik* **19**, 289 (1906); **34**, 591 (1911); *Kolloid-Z.* **27**, 137 (1920).
- <sup>3</sup> Smith, *J. Rubber Res. Inst. Malaya*, Communication no. **243** (in press).
- <sup>4</sup> Guth, *Kolloid-Z.* **74**, 147 (1936).
- <sup>5</sup> Bächle, *Kautschuk* **12**, 210 (1936); *RUBBER CHEM. TECH.* **10**, 675 (1937).
- <sup>6</sup> This is not indicated in the text of Bächle's paper, but has been pointed out to us in correspondence.
- <sup>7</sup> Bächle has not published his data, and the scales attached to his graph are not indicated with sufficient accuracy to enable us to make detailed comparison between his results and ours. The apparent difference in the range of agreement with his theoretical curve could be accounted for, without any appreciable difference in the observations, if in drawing his theoretical curve he used simply d.r.c. by weight in place of  $\phi$ . War interrupted our correspondence before such points could be elucidated.
- <sup>8</sup> If, as used above,  $\phi$  represents the volume concentration of dry rubber, the constant  $k$  might be taken to be an estimate of increase in the volume of disperse phase due to water of hydration

and other adsorbed substances. The introduction of  $k$  into Bächle's equation is however of no help in adjusting this equation to latex data. Fitting

$$\eta = \eta_0 [1 + 2.5\phi / (1 - k\phi) + 7.79\phi^2 / (1 - k\phi)^2]$$

to the data of series 3 by the method of least squares, we obtain  $\log_{10}\eta_0 = -0.057$ ,  $k = 1.29$ . This gives a curve which starts below the observations ( $\eta_0 = 0.88$ , instead of 1.06), crosses them at 26 per cent d.r.c., and continues above them to the highest observation at 66 per cent d.r.c.; a curve which is of no interest whatsoever, and merely shows the inability of the equation to fit the data over the whole range.

<sup>9</sup> Hatzschek, *Kolloid-Z.* **3**, 34 (1911).

<sup>10</sup> Arrhenius, *Medd. K. Vetenskapsakad., Nobelinstitut* **3**, No. 13 (1916).

<sup>11</sup> For graphs showing original data plotted on the scales of centipoises: d.r.c. per cent, see RUBBER CHEM. TECH. **12**, 655 (1939).

# SPECIFIC GRAVITY OF LATEX AND OF RUBBER

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## INTRODUCTION

From observations on specific gravity and dry rubber content of latex, of centrifugal concentrates, and of latex-water mixtures, a number of attempts have been made to deduce the specific gravity of the rubber phase. Such estimates, after allowing for criticisms and adjustments which have been put forward, range from 0.901 to 0.914. But writers have made no attempt to consider how their calculations would be affected by treatments of the latex such as ammoniating and centrifuging, by different ways of evaluating the results, and by variations in temperature. When consideration is given to such matters almost all observations published during the last 20 years are found to be in good agreement one with another.

Specific gravity, the ratio of the mass of a certain volume of a substance, at temperature  $t_2$ , to that of the same volume of water, at temperature  $t_1$ , is commonly designated  $d_{t_1}^{t_2}$ . To avoid excess affixes, when the temperature of the substance does not require to be stated, let:

- $S$  indicate specific gravity relative to water at the same temperature as the observed substance ( $=d_t^t$ ).
- $S'$  indicate specific gravity relative to water at 4° C ( $=d_4^t$ ).
- $\rho$  indicate relative density of water at the temperature of the observed substance.
- $V$  indicate the reciprocal of  $S^1$ .

Let different substances be indicated by subscripts which will usually be obvious. In particular:

- $R$  = the rubber phase in latex
- $S$  = serum
- $L$  = latex = a mixture of rubber and serum
- $LM$  = a mixture of latex and ammonia, etc.

Let  $x$  be the weight concentration of rubber in latex = d.r.c. per cent by weight divided by 100, and

$x'$  be the weight of rubber in 1 ml. of latex at the temperature of observation.

$$R = S_S' | S_R' = S_S | S_R.$$

We will assume that there is no physico-chemical interaction among ingredients of fluids considered in this paper, so that the volume of a mixture is equal to the sum of the volumes of its components, i. e., we assume that the "law of mixtures" is applicable. The magnitude of errors which may be thus intro-



duced is examined in Appendix 1. With this assumption the following formulas may be derived:

$$S_L' = S_s' - (R-1)x' \quad (1)$$

$$= \frac{S_s'}{1 + (R-1)x} \quad (2)$$

and

$$S_L = S_s - (R-1)\rho^{-1}x' \quad (3)$$

$$= \frac{S_s}{1 + (R-1)x} \quad (4)$$

$$V_L = V_s + (V_R - V_s)x \quad (5)$$

Formulas (1) and (2), or (3) and (4), are, with changes in notation, those presented by de Vries<sup>2</sup> and used by Rhodes<sup>3</sup>, except that de Vries ignored the distinction between Equations (1) and (3). Relative to the accuracy of data at present available, differences in numerical value between the two formulas are not important (putting  $\rho=1$  in Equation (3) at 29° C would lead to underestimating  $S_R$  by about 0.0004); but to avoid ambiguity and possible confusion it is advisable to retain the distinction in the formulas; and to avoid bias it should be included in calculations. Equation (5) has been given by van Gils<sup>4</sup>.

Numerical estimates of the constants in these equations have been derived from observed data by the method of least squares (see Appendix 2)<sup>5</sup>.

#### RHODES' DATA (AMMONIATED LATEX)

Rhodes<sup>6</sup> observed 852 samples of ammoniated latex from commercial tasks on nine estates. The dry-rubber contents were fairly evenly distributed from 28 to 50 per cent by weight. Specific gravity was observed at about 29° C, relative to water at the same temperature. In his second paper (1935) Rhodes assumed that Equation (4) would be applicable to ammoniated as well as to fresh latex, and fitted to his data an equation of the form:

$$S_{LM} = \frac{a}{1 + bx_m} \quad (6)$$

where  $a$  and  $b$  are arbitrary constants, and  $x_m$  is d.r.c. in grams of rubber per gram of ammoniated latex. Extrapolating this to  $x_m=1$ , he took as his estimate of  $S_R$ :

$$\frac{a}{1+b} \quad (6a)$$

Observations were made on latex which had been ammoniated by adding, to every 100 ml. of fresh latex, 2.8 ml. of ammonia containing 25 per cent  $\text{NH}_3$  by weight. Let  $v_M$  be the volume of another fluid mixed with unit volume of latex, the specific gravity of the fluid,  $M$ , being  $S_M$ . Then for the circumstances of Rhodes' observations,  $v_M$  is a constant and, following out the implications of the law of mixtures as outlined in the Introduction, we find that Equation (6) is indeed still applicable; but whereas  $b$  remains the same as in (4), viz.,  $(R-1)$ , we now have:

$$a = \frac{S_s + v_M S_M}{1 + v_M}$$

= the specific gravity of a mixture of  $v_M$  ml. of  $M$  with 1 ml. of serum.

Equation (6) therefore represents:

$$S_{LM} = \frac{S_S + v_M S_M}{(1 + v_M)[1 + (R - 1)x_m]} \quad (7)$$

and

$$S_R = \frac{a}{1 + b} + \frac{v_M(S_S - S_M)}{R(1 + v_M)}$$

When the added fluid  $M$  is ammonia ( $S_M$  at  $29^\circ \text{C} = 0.9060$ )  $S_S$  is greater than  $S_M$ , and (6a) would underestimate  $S_R$ . For the conditions of Rhodes' work the error is about 0.003.

Fitting by least squares Equation (7) we obtain:

$$\begin{aligned} S_S &= 1.0228 \pm 0.000919^* \\ S_R &= 0.9097 \pm 0.001137^* \end{aligned}$$

The estimated standard deviation of single observations about the regression is 0.00376%, but this figure may have been substantially inflated by heterogeneity of the data (see below).

Substituting these statistics in (3), we estimate that regression of  $S_L$  on  $x'$  in original fresh latex was:

$$d_{29}^{20} = 1.0228 - 0.1248 x' \quad (8)$$

The standard errors of the coefficients are respectively  $\pm 0.000919$  and  $\pm 0.002405$ .

$S_S$  and  $S_R$  are arbitrary constants, estimated by fitting Equation (7) to Rhodes' data<sup>6</sup> (Table II); they can be assumed to be estimates of the specific gravities of the serum and rubber phases only on the hypothesis that Equation (7) truly represents the physical relationships, (see Discussion later). Their standard errors are estimated from the variation of the data (means of classes of 2 per cent d.r.c.) about the fitted line; they are strictly valid only if variation about the regression can be assumed to be at random. Unfortunately at least two types of systematic errors may be present in Rhodes' data.

(1) Since concentrated ammonia solution is rather volatile and difficult to handle, the actual values of  $v_M$  and  $S_M$  may have deviated systematically from the theoretical values.

(2) The observations on 852 samples from nine estates have been summarized in classes of 2 per cent d.r.c. Table II of Rhodes<sup>6</sup> gives the mean and standard deviation of specific gravities in each class. For heterogeneity of standard deviations about the regression (column 10 of Table II),  $\chi^2 = 94.55$ , with  $n = 10$  (cf. Bartlett<sup>8</sup>), therefore, these standard deviations vary more than can be expected by random sampling. Now samples from each estate are represented in varying proportions in each class, and inspection shows that the five classes which contain samples from estate No. 5 have standard deviations greater than the other six classes. We may therefore presume that, for corresponding values of d.r.c., latices from estate No. 5 differ from others in specific gravity.

The mean square for means of classes about the regression is  $0.1415 \times 10^{-4}$ , whereas the mean variance within classes, also about the regression (not about means of classes), is only  $0.0238 \times 10^{-4}$ . This situation has evidently arisen because means of classes are not independent, for reasons given in the preceding paragraph; therefore in these data a comparison of estimates of variance derived from internal and from external consistency (cf. Deming<sup>10</sup>) is only to

be taken as indicating heterogeneity of the data; it does not indicate a poor fit of the regression.

Unfortunately the original data were lost in the fire at the Institute, so that variation within and between estates cannot now be evaluated. Owing to the heterogeneity of the data, statistics derived from the extant summary may be biased, and valid estimates of error are not obtainable. From the general configuration of the data, we may guess that the average bias is slight; errors of regression coefficients are probably overestimated.

#### DE VRIES' DATA (FRESH LATEX)

The principal data on which de Vries' conclusions have been based<sup>11</sup> give d.r.c. and  $d_t^t$ , at an average temperature of about 27° C, for two groups of trees in an experimental area on 19 or 20 successive days. Following a resting period, the d.r.c. was 40-45 grams per 100 ml., fell rapidly to below 30, and then more gradually to about 18 grams per 100 ml. Fitting to these data Equation (3), we obtain:

$$\text{from Table IV: } d_{27}^{27} = 1.0202 - 0.1204 x' \quad (9)$$

$$S_R = 0.9109 \pm 0.00144; S_S = 1.0202 \pm 0.00069;$$

$$\text{from Table V: } d_{27}^{27} = 1.0218 - 0.1239 x' \quad (9a)$$

$$S_R = 0.9094 \pm 0.00193; S_S = 1.0218 \pm 0.00071.$$

The mean standard deviation of single observations about the regressions is 0.00078, and the standard errors of the regression coefficients (0.1204 and 0.1239) are 0.00230 and 0.00286, respectively.

These results are in excellent agreement with Equation (8), evaluated from Rhodes' data. Comparison of the mean estimates of  $S_S$  and  $S_R$  is as follows:

	$S_S$	$S_R$
de Vries 27° C	1.0210 $\pm$ 0.00050	0.9102 $\pm$ 0.00120
Rhodes 29° C	1.0228 $\pm$ 0.00092	0.9097 $\pm$ 0.00114
Difference	-0.0018 $\pm$ 0.00105	0.0005 $\pm$ 0.00166
Expected difference for 2° C (App. 3)	} $\cong$ -0.00001	
		0.00070

Differences are not statistically significant. Such as it is, the difference in  $S_R$  is in the direction and of the magnitude to be expected, owing to the difference in temperature of 2° C between the average conditions of the two sets of observations. The difference in  $S_S$ , however, while not disproving the hypothesis that  $S_S$  is equal in the two sets (P about 0.12), is also in accordance with the suggestion put forward by other workers that the specific gravity of serum may vary with origin more than does that of the rubber phase.

While admitting the possibility of small differences in the specific gravity of serum, it is evident that any disagreement between the conclusions of the two authors is not inherent in the data.

The basis of the method used by de Vries<sup>12</sup> to estimate  $S_R$  was different. After coagulating fresh latex with  $v_A$  ml. of 2.5 per cent acetic acid per ml. of fresh latex, he observed the specific gravity of the acidified serum ( $S_{SA}$ ), and com-

puted values of  $S_R$  and  $S_S$  for each sample separately from the following formulas, which can be derived as indicated in Section I:

$$S_R = \frac{S_{SA}x'}{[S_{SA}(1+v_A) - S_L - v_A S_A]\rho + x'} \quad (10)$$

$$S_S = \frac{S_{SA}(S_L\rho - x')}{[v_A(S_A - S_{AS}) + S_L]\rho - x'} \quad (11)$$

The values of  $S_R$  thus estimated<sup>13</sup> from data given in Tables III to V (*loc. cit.*) varied inversely with the d.r.c. of the latex from 0.910 to 0.925. They are graphed in Figure 1.

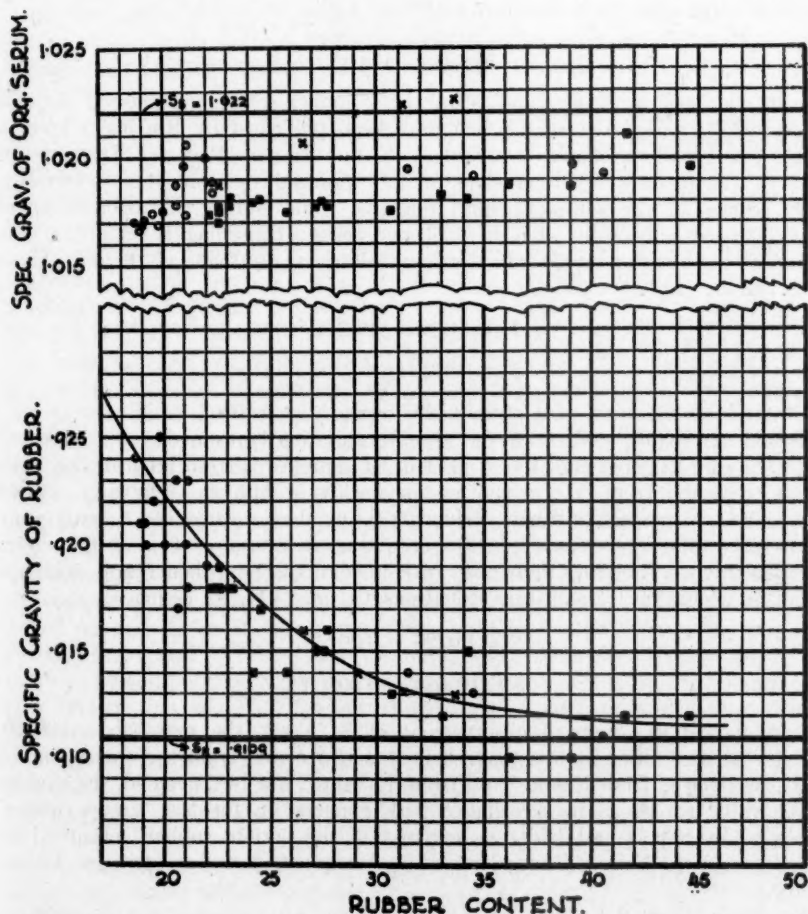


FIG. 1.—Relation between specific gravity of rubber and serum phases and d.r.c. (g. per ml.) of latex. Data from de Vries<sup>13</sup>.

× Table III,    ■ Table IV,    ○ Table V.

On the hypothesis that  $S_R$  tends towards a constant for high values of  $x'$ , both this asymptotic value and the standard deviation of the observations may be estimated from an equation of the form:

$$y = k + (a + bx' + cx'^2)^{-1}$$

A first approximation to the least squares solution is:

$$S_R = 0.91092 + (634.68 - 6271.2 x' + 17694 x'^2)^{-1} \quad (12)$$

with standard deviation of observations about the regression = 0.00171; whence the limiting value of  $S_R$  for high d.r.c. is estimated to be  $0.9109 \pm 0.00091$ .

The estimates of  $S_S$  are also shown in Figure 1, where it can be seen, without the labor of fitting a complex curve, that for high values of  $x'$  they tend towards a value somewhere between 1.020 and 1.022.

#### OTHER DATA

I am indebted to Rhodes and Sekar for a further set of unpublished data on latex (other characteristics of which have been published by Rhodes<sup>14</sup>) from a single small-holding, under the control of the Rubber Research Institute of Malaya. There were 29 observations for 29 tapping days, from May to October, 1938. Since all the samples came from the same source, variation is small (d.r.c. varied only from 36.5 to 42.3 per cent); consequently errors in the estimates of the constants in which we are interested are relatively high<sup>15</sup>. These observations (at about 29° C) gave:

$$S_S = 1.0212 \pm 0.0190$$

$$S_R = 0.9113 \pm 0.0267$$

and standard deviation of  $S_L$  about the regression = 0.00363.

Scholz and Klotz<sup>16</sup> observed the specific gravities (presumably  $d_t^t$  at about 29° C) and d.r.c. (per cent by weight) of 91 samples of fresh latex drawn from single trees and from tree groups on one estate in Malaya. The d.r.c. varied from 30 to 56 per cent. When evaluating d.r.c., they washed the coagula more thoroughly than is customary<sup>17</sup>, thus obtaining an estimate of what they term "crepe content". Reading their observations from the published graph (perhaps none too accurately) and fitting Equations (3) and (4), we estimate:

$$S_S = 1.0228 \pm 0.00172$$

$$S_R = 0.9084 \pm 0.00209$$

with standard deviation of observations of  $S_L$  about the regression = 0.00209. These statistics differ by less than their standard errors from the corresponding statistics derived from Rhodes' and from de Vries' data but, even so, the slightly lower value for  $S_R$  is in accordance with expectation for the "crepe rubber" observed by Scholz and Klotz in contrast to the "crude rubber" observed by Rhodes and de Vries. (Compare results for purified and centrifugal latices, below.)

Stamberger and Schmidt<sup>18</sup> purified rubber by cataphoresis, and investigated the specific gravity of dispersions of this purified rubber in 0.6 per cent ammonia at 18° C. From this they estimated, by extrapolation on a linear regression of density on d.r.c. per cent by weight, that the density of the disperse phase was 0.905. But as we have already seen, this regression is not



linear, a fact which can be empirically demonstrated by graphing their data<sup>19</sup>. Fitting an equation of form (5) we obtain:

$$V' = 1.0034 + 0.09706x$$

with standard deviation about regression = 0.0036. This gives  $S_R' = 0.9087 \pm 0.00059$  at 18° C. For pure rubber obtained by drying, they observed the practically identical value  $d_4^{18} = 0.909$ . Adjusted by the figures for expansivity of rubber reported by Bekkedahl<sup>20</sup> this becomes 0.9045<sup>21</sup> for  $d_4^{25}$ ; it is therefore slightly lighter than rubber purified by chemical methods and observed by McPherson<sup>22</sup> to have  $d_4^{25} = 0.9060$ <sup>23</sup>. (See further page 494.)

### CENTRIFUGAL CONCENTRATES

Rhodes<sup>6</sup> and van Gils<sup>4</sup> have observed the specific gravities of centrifugal concentrates and have derived from the results estimates of  $S_R$  by extrapolating regressions of specific gravity on d.r.c. between the skim and concentrate from individual parent latices. This procedure would be justified if the serum and rubber phases were homogeneous fluids which could not be centrifugally separated into fractions of different density; but if the serum, or the rubber phase, or both, can be separated into sub-fractions, it is meaningless to extrapolate a regression of specific gravity on d.r.c. beyond the observed values of the skim and concentrates themselves.

For example: Suppose a skim had 15 per cent d.r.c., with  $S_S = 1.020$ , and the cream had 55 per cent d.r.c., with  $S_S = 1.010$ ,  $S_R$  in both being 0.906, extrapolation as described would lead to estimates of specific gravity at 0 and 100 per cent d.r.c. of 1.0222 and 0.8961, respectively.

It cannot be proved, from data at present available, that either the serum or the rubber phase can be separated centrifugally into subfractions; but a hypothesis that serum at least can be fractionated enables all the relevant data to be reconciled; whereas a hypothesis that the respective densities of serum and of rubber are equal in both skim and concentrate leads to conflicting estimates of the specific gravities of these phases.

Van Gils apparently assumed that the gravitational settlement of the latex was sufficient to reduce the serum to a homogeneous fluid which would not be further separated; Rhodes apparently assumed that after the deposition of the sludge in the centrifuge, the remaining serum would be homogeneous. It seems unlikely however that separation would be complete in either case, and further separation between the remaining fluids might be anticipated. There may also be differences between the two fractions of the rubber phase, since it is known that the skim tends to have smaller particles, which may carry a higher proportion of adsorbed substances.

Rhodes<sup>6</sup> (Table VIII) gives the specific gravities and the d.r.c. of the skim and cream from one parent latex and also for 12 mixtures of these. Since they are mixtures of fluids which had formerly been mechanically separated, they must obey the law of mixtures; indeed Equation (4) fits the observations very closely, the standard deviation of single observations about the fitted regression being only 0.0004. The regression is:

$$S = 1.0171(1 - 0.1280 x)^{-1}$$

and its extrapolated values at  $x=0$  and 1 are  $1.0171 \pm 0.00035$  and  $0.9017 \pm 0.00046$  respectively. In view of other evidence it is difficult to accept the

latter figure as a likely value for  $S_R$  (compare figures derived for a theoretical example above), and there is a *prima facie* case for suspecting that a hypothesis which leads to this as an estimate of  $S_R$  may be invalid.

Van Gils' experimental material differed from that of Rhodes in that, before centrifuging, he diluted his latex to five per cent d.r.c. with 0.25 per cent ammonia, whereas Rhodes centrifuged his latex without dilution. In the following discussion "serum" refers to the dispersion medium comprising a mixture of serum and the water resulting from dilution.

Assuming that the reciprocal of the specific gravity of a rubber serum mixture is given by the expression:

$$V = V_S + (V_R - V_S)x$$

where  $x$  is the d.r.c. of the mixture, van Gils estimated  $V_R$  by taking the values of  $V$  and of  $x$  observed for the skim and concentrate from one parent latex, and solved the two equations thus formed for the two unknowns  $V_R$  and  $V_S$ . As pointed out above, this assumes that  $V_S$  and  $V_R$  have the same values in the skim and in the concentrate; if this assumption is incorrect the consequent error would be in the direction of underestimating  $V_S$  and overestimating  $V_R$ . We may therefore take van Gils' figure, *viz.*,  $0.9042 \pm 0.00009$ , as an estimate of the lower limit for the mean specific gravity of the rubber phases in his concentrates. The corresponding estimate of the mean specific gravity of the sera is 1.0013.

On the other hand if we consider the hypothesis that the specific gravity of serum in a concentrate may be less than that of the serum in the corresponding skim, we cannot then estimate  $V_R$  and  $V_S$  from existing data, but we can assume that the serum in a concentrate cannot be less dense than water, that is,  $V_S$  is not greater than unity; and substituting  $V_S=1$  in the above equation we can obtain estimates of the lower limit of  $V_R$  for each concentrate. This procedure gives:

$$S_R \leq 0.9052 \pm 0.00016$$

Adjusted for temperature, these limits become, at 29° C, 0.9045 and 0.9055. The potential error in van Gils' data is less than in Rhodes' data discussed above, because dilution with water reduces the possible difference of specific gravities of sera in the two fractions even if all serum solids were thrown out with the skim, and because the greater difference in rubber contents between concentrates and skim (51.37 per cent in van Gils' data compared with 41 per cent in Rhodes' data) reduces the extent to which differences may be exaggerated by extrapolation.

De Vries<sup>24</sup> has pointed out that  $S_R$  as estimated by van Gils for each sample is correlated with the d.r.c. of the original (ammoniated) latex. The regression coefficient of  $S_R$  on  $x_m$ , in the units adopted throughout this paper, is  $-0.00532 \pm 0.00161$ , and is highly significant ( $P$  less than .01). It appears therefore that the observed rubber content is still contaminated with heavier ancillary substances, more or less in proportion to the amount of serum in the original latex.

For van Gils' 23 concentrates, the regression of reciprocal of specific gravity on d.r.c. is:

$$V = 0.9973 + 0.1099x \\ \pm 0.0038$$

The slope is greater (although not significantly so) than the mean slope between skims and concentrates, *viz.*, 0.1072.

Rhodes<sup>6</sup> (Table VII) reported specific gravities of 68 Dunlop centrifugal concentrates, for which the regression of the reciprocals on d.r.c. is:

$$V = 0.9508 + 0.1821x \\ \pm 0.0142$$

The slope of this regression is substantially steeper than any others reviewed in this paper; and extrapolation to  $x=0$  and 1 gives 1.0518 and 0.8827, respectively; figures which cannot be accepted as at all likely for values of  $S_S$  and  $S_R$ .

The only assumption compatible with these data therefore seems to be that the density of serum and (or) of observed rubber varies with the degree of concentration. Under these circumstances no estimate of the specific gravities of the phases can be obtained from a regression among ordinary centrifugal concentrates.

For further research, consideration might be given to repeated dilution and centrifuging of samples of latex from different sources. After two or three dilutions it would probably be safe to assume that the disperse medium was homogeneous in both skim and concentrate.

#### DISCUSSION

In the discussion of de Vries' data and in Figure 1, we have seen that direct evaluation of the specific gravity of the crude rubber phase in individual samples of latex indicated values of  $S_R$  from 0.925 to 0.910, depending on the d.r.c. of the latex. Pending more chemical and physical data to elucidate the reason for this variation, further statistical work on a speculative basis is scarcely worth doing. Meantime, for the sake of discussion, let us assume that the specific gravity of the rubber phase may be constant, but may seem to vary owing to association with serum solids of greater specific gravity (as was suggested by de Vries<sup>25</sup>, and is corroborated by observations on purified latex). When estimating  $S_R$  in such circumstances, Rhodes' method (by extrapolation of the regression  $S_L$ :d.r.c.) would be affected only by the error in the d.r.c., and might either over- or underestimate  $S_R$ , depending on the relation between d.r.c. and the amount of serum solids precipitated. De Vries' method would be affected by errors both in d.r.c. and in specific gravity of the serum; overestimates of d.r.c. ( $x'$ ) and underestimates of  $S_{SA}$  would both tend to increase the estimate of  $S_R$ .

Data at our disposal do not make possible a really satisfactory evaluation of average figures for  $S_S$  and  $S_R$ ; various estimates derived in Sections II to IV are of unequal value, and there is no way of assigning to them rationally determined weights. The work of de Vries<sup>26</sup>, in which the standard deviation of single observations about the regression was only 0.0008, shows that quite a few observations can yield accurate figures for any given group of trees. Therefore, if observations be properly planned, it should not be difficult to obtain evidence and quantitative estimates of changes in the regression of  $S_L$  on d.r.c. for different estates (or fields), manures, clones, etc. For the solution of problems such as those discussed below, the regression coefficients should be evaluated to four decimal places, with attention to temperature (Appendix 3).

Meantime available data indicate that the relative specific gravity ( $d_4^{20}$ ) at 29° C of the "crude rubber" phase<sup>27</sup> in latex may be about 0.910, of undiluted fresh serum about 1.022. For a purified rubber phase  $d_{20}^{20}$  appears to be about 0.9056.

Observations on the specific gravity of solid rubber, adjusted for temperature to give  $d_{29}^{29}$ , are as follows (derived from the review by Wood<sup>28</sup>):

	Commercial raw rubber	Purified rubber
Selected by Wood as most reliable value.....	0.912	0.9072
Mean of 21 raw and of 5 purified values.....	0.914	0.913
Range of 21 raw and of 5 purified values.....	{ 0.906 0.929	0.906 0.922
Stamberger and Schmidt <sup>18</sup> (see above).....	—	0.9057

These figures indicate specific gravities of both crude and purified rubber about 0.002 greater than our estimates of the more or less corresponding phases in latex. There is no way of telling at present in how far this may be due to differences in the material observed rather than to a change of state. We have shown above (Section IV) that in at least one experiment (Stamberger and Schmidt<sup>18</sup>) purified rubber had the same density in both dispersed and solid states. It is possible, however, although we have no reason to suppose it at all likely, that changes from the natural state in raw latex may already have taken place during purification by cataphoresis.

Within the limits of accuracy of our data, the "law of mixtures" appears to be adequate as an empirical rule for estimating the specific gravities of latices of varying concentrations (=mixtures of rubber and serum) and of mixtures of latex with other fluids, such as water, ammonia, and dilute acetic acid solutions. Pending more adequate experimental treatment, the application of this law, along with the above estimates of  $S_R$  and of  $S_S$ , may enable us to make intelligent estimates on some outstanding problems.

A. The original object of this investigation was to seek data on which to found a conversion table between d.r.c. per 100 ml. of latex and d.r.c. per cent by weight. Given  $S_R=0.910$  and  $S_S=1.022$  the conversion formula at 29° C is:

$$x = \frac{x'}{1.018 - 0.1231 x'}$$

A few typical values are shown in Table I. It must be remembered, however,

TABLE I

TABLE FOR CONVERTING GRAMS OF RUBBER PER 100 ML. TO D.R.C. PER CENT BY WEIGHT IN UNDILUTED LATEX AT 27-29° C

Grams per 100 ml.....	15	20	25	30	35	40	45	50
Per cent by weight.....	15.01	20.14	25.33	30.58	35.90	41.30	46.75	52.28

that this relationship is subject to alteration for varying values of  $S_R$  and  $S_S$ , and is inapplicable when latex is mixed with an unknown quantity of water. (A somewhat similar table, but with the addition of per cent by volume and based on  $S_R=0.914$ ,  $S_S=1.020$ , has been given by de Vries<sup>29</sup>.)

B. The main purpose of Rhodes' work was to prepare a table of specific gravities of ammoniated latex. But in estate practice latex is usually ammoniated with gas, whereas Rhodes' samples were treated with ammonia in solution. What may be the effect on specific gravity of these different procedures?

Supposing that the specific gravity of ammonia water may be estimated by the mixing law as a mixture of water with a hypothetical liquid ammonia, and given that the specific gravity of one-per-cent ammonia is  $d_4^{29}=0.9920$ , then



the specific gravity of the hypothetical liquid ammonia is  $d_4^{20}=0.7113$ . For a latex of specific gravity 0.975<sup>30</sup> the amount of ammonia gas to be added to 1 ml. of latex to give a concentration of 0.5 per cent ammonia would have a hypothetical liquid volume of  $0.975\rho/(199\times 0.7113)=0.00686$  ml. Whence, using the values of  $S_s$  and  $S_R$  given by Rhodes' data, we estimate that in Equation (6) (and in the corresponding equation of form 3) for ammonia "gassed" latex,  $a=1.0207$ ; whereas for the equations fitted direct to Rhodes' data,  $a=1.0195$ .

It seems likely, therefore, that the increase in specific gravity for latex preserved with gaseous ammonia over that prepared with concentrated liquid ammonia will be of the order of 0.0012 when compared on the basis of grams per 100 ml. (or pounds per gallon), or 0.118 per cent when compared on the basis of per cent of rubber by weight. Pending further direct observations, the figures for specific gravity in Rhodes' table should be multiplied by 1.00118 when intended for use with latex ammoniated with gas.

C. We may consider the problem of estimating d.r.c. from specific gravity. The method is chiefly of interest when specific gravity can be determined with a hydrometer; a thing which can be done for undiluted fresh latex only when the d.r.c. is less than 20 to 24 per cent. To overcome this difficulty, a latex of higher d.r.c. is commonly diluted with water, and the d.r.c. is estimated from the specific gravity of the latex-water mixture.

TABLE II

Rubber content of latex used for calibrating hydrometer; g. per 100 ml. (= 100 $x'$ )	Sp. grav. ( $d_{20}^{20}$ ) of latex-water mixture having 15 g. per 100 ml. (= $S_{LW}$ )	Latexes containing originally 100 $x'$ g. per 100 ml., when mixed with water so that the mixture has a sp. grav. equal to that given in the 2nd column, may be expected to have rubber contents as follows:						
		100 $x'$						
		25	30	35	40	45	50	55
30	.9925	21.2	15.0	12.4	11.0	10.1	9.5	9.0
35	.9909	25.6*	18.1	15.0	13.3	12.2	11.4	10.9
40	.9897	28.9*	20.5	16.9	15.0	13.8	12.9	12.3

\* Impossible cases, for water would require to be *withdrawn* from the latex to satisfy the conditions.

Unfortunately, despite warnings in the literature, there is still in many quarters a tendency to assume that a Metrolac, Simplexometer or Latexometer measures d.r.c. directly. This is incorrect; these instruments can measure nothing except relative specific gravity. If the scale appears to give a reading in terms of d.r.c., this merely means that the figures marked on the instrument incorporate a more or less arbitrary conversion table relating specific gravity to d.r.c. To avoid confusion the real nature of such tests should be kept clearly in mind. Since water and serum differ in specific gravity, there can be no one-to-one correspondence in latex-water mixtures between specific gravity and d.r.c. The point has been fully expounded by de Vries<sup>26</sup>, and he<sup>31</sup>, Hartjens<sup>32</sup> and Rutgers and Maas<sup>33</sup> have demonstrated empirically that direct readings from Metrolacs and Latexometers in latex-water mixtures are unreliable.

A modified procedure sometimes used to obtain a latex-water mixture of approximately standard d.r.c., usually 1.5 lbs. per gallon, is to adjust a hydrometer (or Metrolac, etc.) to come to rest at a given mark when inserted in a particular latex-water mixture of the required d.r.c. Then on future occasions, when a latex is to be diluted to this standard, it is mixed with water until the hydrometer stands at the mark. The method will serve well for latex similar to the latex used for calibration. Otherwise it may give results which are appreciably in error as shown in Table II.



As a rough empirical test of these deductions, Hastings tried out this procedure on eight latices having initial d.r.c.'s of 28-39 per cent. I am indebted to him for the following figures:

d.r.c. of original latex g. per 100 ml.....	28.2	28.4	29.5	33.8	34.9	37.9	38.4	38.6
d.r.c. of latex-water mixture when								
Metrolac read 15 (approx.*) g. per								
100 ml. ....	—†	—†	—†	15.8	15.1	13.5	13.6	14.1

\* Estimated from readings at nearby concentrations.

† No reading with Metrolac obtainable.

These observations agree well with the above table if the Metrolac used was calibrated in latex of about 35 per cent original d.r.c.

By the methods set forth in this paper, the specific gravity of a latex-water mixture may be given by:

$$S_{LW} = \frac{1}{1+d_v} \left\{ d_v + S_S - (R-1)\rho^{-1}x' \right\} \quad (13)$$

$$= \frac{1}{1+d_v} \left\{ d_v + \frac{S_S}{1+(R-1)x} \right\} \quad (14)$$

$$= \frac{(1+d_w)S_S}{1+d_wS_S+(R-1)x} \quad (15)$$

where  $d_v$  = dilution factor measured as  $\frac{\text{volume of water}}{\text{volume of latex}}$ ,

$d_w$  = dilution factor measured as  $\frac{\text{weight of water}}{\text{weight of latex}}$ ,

$x'$  = g. rubber per ml. latex = lbs. per gallon  $\times 0.099886$  (lbs. per gal. =  $10.0114x'$ ).

$x$  = weight of rubber/weight of latex = d.r.c. per cent by weight  $\div 100$ .

Inserting our estimates of  $S_R$  and  $S_S$ , and (in 13) the value of  $\rho_{29}$ , and rearranging, we obtain as formulas to estimate d.r.c. from specific gravity at about 29° C:

$$x' = \frac{1.022 + d_v - (1+d_v)S_{LW}}{0.1236} \quad (13a)$$

$$x = \frac{1.022 + d_v - (1+d_v)S_{LW}}{0.1231[(1+d_v)S_{LW} - d_v]} \quad (14a)$$

$$= \frac{(1+d_w) - (.9785 + d_w)S_{LW}}{0.1204S_{LW}} \quad (15a)$$

Since one volume of latex:two volumes of water ( $d_v=2$ ) is a dilution commonly used, we give in Table III values of the d.r.c. for varying values of specific gravity at this dilution. Tables for other dilutions can be easily prepared from the above equations.

Given equal errors in measuring  $S_{LW}$ , the error of estimating d.r.c. of the latex-water mixture is independent of the amount of dilution; but errors of estimating d.r.c. of the original latex will be increased in proportion to the dilution of the mixture, since observed values must be multiplied by  $(d+1)$ .

If workers wish to use specific gravity as a reliable guide to d.r.c. of latex and of latex-water mixtures, they need more accurate determinations of  $S_s$  and  $S_R$  and of their variation with time and place. If, as Rhodes' figures suggest,  $S_s$  and  $S_R$  are found to vary significantly with locality, but do not change much for any given source of latex over reasonably long periods of time, it would be easy for an estate to ascertain the constants and to prepare tables for its particular conditions.

The accuracy obtainable will depend very much on the accuracy of calibrating hydrometers and on the care with which they are used. Existing instruments and usage apparently leave much to be desired. For example, two instruments used by Hartjens<sup>32</sup> and by de Vries<sup>34</sup> gave readings of specific gravity differing by 0.002; and there is reason to fear that instruments are no more standardized today. Temperature "corrections" (for instruments and tables at present in use,

TABLE III

ESTIMATED RELATIONSHIP BETWEEN SPECIFIC GRAVITY OF FRESH LATEX DILUTED WITH TWICE ITS VOLUME OF WATER AND DRY-RUBBER CONTENT OF ORIGINAL LATEX

Relative specific gravity at 29° C of 1:2 latex- water mixture	Dry-rubber content of original latex	
	Lbs. per gal.	Per cent by weight
0.986	5.185	54.28
0.987	4.942	51.57
0.988	4.699	48.88
0.989	4.456	46.21
0.990	4.213	43.55
0.991	3.970	40.91
0.992	3.727	38.29
0.993	3.484	35.68
0.994	3.241	33.09
0.995	2.998	30.52
0.996	2.754	27.96
0.997	2.511	25.41
0.998	2.268	22.88
0.999	2.025	20.37
1.000	1.782	17.87
1.001	1.539	15.39

Note: lbs. per gal. = g. per 100 ml.  $\times$  0.100114; g. per 100 ml. = lbs. per gal.  $\times$  9.9886.

cf. de Vries<sup>35</sup>) are greater than 0.0003 per ° C, and consequently are often important.

Theoretically a hydrometer scale can be prepared to give direct readings of d.r.c., if used in latex diluted with a fluid having a specific gravity of 1.022. But the technical difficulties of maintaining stocks of such a fluid would probably be troublesome, and on other grounds it is undesirable to have anything except specific gravity ( $d_4^t$ ) graduations on a hydrometer. In the words of Stott<sup>36</sup>, whose article may be consulted for fuller information on the theory and use of hydrometers: "For very rough work there may sometimes be an advantage in a hydrometer graduated to indicate the property of a liquid in which the user is directly concerned; [but] in most cases the necessity arises sooner or later of using tables of correction in conjunction with the hydrometers. Once this necessity arises, it is equally easy and more satisfactory for all purposes to use a standard type of instrument, graduated to indicate *densities*." A thorough review of the problem, with plans for a revision of instrument scales and tables, should incorporate an investigation of surface tension effects in rubber-water mixtures.

When latex has been diluted with unknown amounts of water, *e. g.*, by rain, only a very rough estimate of d.r.c. can be obtained from specific gravity.

## APPENDIX 1

### THE MIXING LAW IN LATEX PROBLEMS

If there is no physical or chemical interaction of two or more substances (*i, j . . .*) when mixed, the specific gravity of a mixture, relative to water at 4° C, must be:

$$S'_{ij} \dots = \frac{w_i + w_j + \dots}{v_i + v_j + \dots}$$

where *w* is measured in grams and *v* in milliliters. But if the volume of the mixture is not equal to  $v_i + v_j + \dots$ , its specific gravity will not conform exactly to this law. We have assumed that the law is valid for mixtures of all substances used in the work discussed, and it is advisable to obtain some idea of the magnitude of errors made by this assumption.

De Vries<sup>27</sup> has presented data to indicate that the assumption is true, within the range of a fairly low experimental error, for mixtures of latex and water; and for serum and acetic acid<sup>28</sup>.

**LATEX AND AMMONIA:** (1) We assume by hypothesis that ammonia has no influence on the specific gravity of the rubber phase, this being one of the points which require to be tested by observations on fresh and on ammoniated latex. So far as present evidence goes, there is no indication that this hypothesis may be untrue. For a critical test, however, it would be desirable to observe both fresh and ammoniated samples from the same parent latices.

(2) There is, so far as I know, no data available to test whether or not the law provides a reasonable approximation for mixtures of ammonia with latex regarded in bulk as a homogeneous fluid, or with serum, assuming the hypothesis that the rubber phase may be unaffected. Such data might be obtained along with a critical test of (1) above. Meantime we may note the error which would be made in estimating the specific gravity of one per cent ammonia as a mixture of 1 gram of 25 per cent ammonia with 24 grams of water. The following are values for  $d_4^{20}$ :

	Estimated by "mixing law"	True value, given by "Critical Tables"	Difference
At 15° C.....	0.9952	0.9948	0.0004
At 20° C.....	0.9942	0.9939	0.0003
At 25° C.....	0.9930	0.993	0.000 +

Values of  $d_4^{20}$  for solutions from 1 to 30 per cent ammonia, obtained by extrapolation from Critical Tables<sup>29</sup> are described by the formula:

$$0.99679 - 0.46358x + 0.46526x^2 - 0.48846x^3 \quad (16)$$

where *x*=proportionate concentration of ammonia by weight. By the "mixing law" for mixtures of 25 per cent ammonia ( $d_4^{20}=0.9023$ ) with water we would have:

$$S_4^{20} = 0.99597(1 + 0.0041525x)^{-1} \quad (17)$$

(17) is slightly greater than (16) for  $x=0.02$  to 0.25, slightly less than (16) from 0 to 0.02. At  $x=0.01$ , the difference is 0.00035; at  $x=0$ , (16) is too high

by 0.00082. Between  $x=0.005$  and 0.01, the region of especial interest to us, it is not possible with available data to say which equation may be more correct.

There remain for consideration changes caused by precipitation of serum solids by ammonia. I know of no data, however, to show the effect of these on the specific gravity of latex, so long as the precipitates are held in suspension.

In the data discussed in this paper, there is no evidence against the mixing law so long as all components are retained in the mixture; but when ammoniated latex is clarified by gravitational settlement the specific gravity may be lowered by 0.001 to 0.005 (Rhodes<sup>6</sup>). This will suggest further points for investigation to anyone who may conduct a thorough research on the subject.

## APPENDIX 2

### NOTE ON STATISTICAL METHODS USED TO FIT REGRESSION LINES

Although Equations (4) and (2) can be fitted directly to a set of observations, it is much simpler to work with reciprocals of specific gravities and fit the linear Equation (5). Consequent changes of weighting are negligible. It is also possible to calculate  $x'=xS_L\rho$  and fit Equation (3) or (1), but this method is less desirable, because it introduces experimental errors in the observation of specific gravities into both variates.

In all computations we have treated specific gravity (or its reciprocal) as the dependent variate ( $y$ ), and d.r.c. as the independent variate ( $x$ ); and have minimized vertical deviations from the fitted curve. Theoretically this means that observations of  $x$  have been assumed free from error relative to the error of observations of  $y$ .

For theoretically more correct treatment we must recognize two sources of variation: (a) errors of observation, which, although not ascertained, may be of more or less equal magnitude for both variates; and (b) biological variation, independent of the average relationship between the two characters. Proper treatment of observational errors (Group a) should take account of the error in both variates (see, for example, Deming<sup>10</sup>); whereas the treatment of biological variation from the mean curve depends on whether the argument of the investigation calls for the regression of  $y$  on  $x$  or of  $x$  on  $y$ . When studying specific gravity for varying d.r.c., the former (as computed) is correct; but when we go on, as was done in the Discussion, to consider the estimation of d.r.c. from specific gravity, we should use the regression of  $x$  on  $y$ .

However, in work here reported the residuals are usually sufficiently small so that the distinction between our more or less false solutions and the correct ones can be assumed to be negligible, or at least to be less than variations which might be introduced by different methods of averaging the findings of different workers, a problem with which we have dealt in an entirely arbitrary manner. In the principal groups of data covering a reasonably wide range of d.r.c., the alternative extreme assumption, *viz.*, that  $y$  was entirely free from error, would reduce the estimates of  $S_p$  by 0.0002 (Rhodes' data) or 0.0004 (de Vries' data). For Stamberger and Schmidt's data, the alteration would be only  $2.4 \times 10^{-5}$ .

## APPENDIX 3

### EFFECT OF TEMPERATURE ON SPECIFIC GRAVITY OF LATEX

Most writers, reporting data for specific gravity of latex, have failed to indicate the temperature at which observations were taken, and whether specific

gravity is referred to water at the same or at some fixed temperature. Among seven text books which quote figures for specific gravity of latex, and sometimes for the rubber and serum phases, I have seen only one<sup>40</sup> mention of temperature conditions. Some give false information, since they quote figures for  $d_4^t$  under the title of "density".

That the temperature conditions are not negligible may be illustrated by the specific gravity of purified rubber (estimated from figures given by Wood<sup>28</sup>) as follows:

$t$	$d_4^t$	$d_4^t$
15° C	.9121	.9129
30° C	.9030	.9069

Thermal variations of the specific gravity of latex are smaller, being intermediate between those for rubber and for water, but these figures are relevant since debate centers largely around the derivation of estimates for the rubber phase.

The confusion is the more remarkable because workers in latex technology have to deal with both tropical and temperate conditions, and differences between observations at the two places might have been expected to attract attention. As an example of the existing confusion, we may instance discussion on the comparison of Rhodes' data with the specific gravity table adopted by the Rubber Trade Association, London (Rhodes<sup>6</sup>; de Vries<sup>25</sup>; Stevens and Stevens<sup>41</sup>). Although Rhodes' table was constructed for  $d_4^t$  ( $t=29^\circ$  C) and the R.T.A. table, if correct for its purpose, is for  $d_{40}''$  ( $t_0=62^\circ$  F= $16.7^\circ$  C), not one of the three contributors to the discussion noted that the two tables should differ on account of temperature effects, even if there were no other variables as well<sup>42</sup>.

Almost the only data on the variation of volume (or of density) of latex with temperature seem to be those given by Vernet<sup>43</sup>. Unfortunately he has published only a mean curve for an unspecified number of latices, and gives no information on expansivity of latices of varying concentrations except the remark: "The curves which we have been able to obtain with latices of different concentrations do not vary sensibly among themselves." His mean curve indicates that the coefficient of expansivity at  $25^\circ$  C was 0.00055, which, although higher than we might expect, is possible for rich latex. His figures, however, increase surprisingly with temperature, and at  $29^\circ$  C his coefficient of expansivity (0.00075) is greater than that for pure rubber (0.000673; Bekkedahl<sup>21</sup>). (Vernet's curve<sup>44</sup> shows  $\frac{d}{dt} \left( \frac{1}{v} \frac{dv}{dt} \right)$  of latex =  $50 \times 10^{-6}$ ; compare  $17 \times 10^{-6}$  for water, and  $0.7 \times 10^{-6}$  for purified rubber.)

In the "International Critical Tables" (II, 255 Table 2), and in Dawson and Porritt<sup>45</sup>, Table 14, purport to give the "Temperature coefficient of specific gravity of latex" based on data by Hartjens<sup>32</sup>. Actually, these tables are of little use except to illustrate the chaotic state of the subject. The two columns (or rows) are entitled, respectively, "Sp. gr. of latex" and "Correction per  $1^\circ$  C." Since the subject of the tables is variation of specific gravity with temperature, a reader might be pardoned if, in the absence of further guidance, he expects different figures for specific gravity to be associated with varying temperatures. But in the first column, specific gravity is really only a secondary character,



which is intended to imply "d.r.c., as indicated by specific gravity". A reader might be able to infer this from the preceding table in each book, but only knowledge of the original paper, and acquaintance with the hydrometers which were the immediate subject of discussion, can disclose that specific gravity is defined as  $d_t^t$ ,  $t$  being taken to be constant at about 29° C. The figures under the heading "Correction per 1° C" were originally given as correction for hydrometer readings to estimate  $d_t^t$  at the temperature (about 29° C) for which a hydrometer had been graduated<sup>46</sup>. This, however, is not the same as the "temperature coefficient of specific gravity", although it is nearly equal to it if specific gravity be defined as  $d_t^t$ . Therefore, in so far as the table has any meaning, its two parts are based on different (and undisclosed) definitions of specific gravity for which (as Table IV shows) the temperature coefficients are not at all similar. Finally, since no temperature conditions are stated, there is no warning to readers who may be concerned with room temperatures in a temperate climate, or with high temperatures in some industrial process, that the figures are derived only from observations at tropical room temperatures near 29° C.

If a hydrometer, graduated to show  $d_t^t$  when immersed in a fluid at  $t^\circ$  C, reads  $u_t$  when used at  $t'^\circ$  C, then the true value of  $d_{t'}^{t'}$  is given by:

$$\frac{u_t \rho_t}{\rho_{t'} \{1 + \alpha(t' - t)\}}$$

$\alpha$  being the coefficient of cubical expansion of the material of which the hydrometer is made (cf. Stott<sup>47</sup>). Assuming that all observations were made with glass hydrometers having  $\alpha = 26 \times 10^{-6}$ , we may use this formula to obtain, from Hartjens' hydrometer corrections, estimates of thermal changes in specific gravity for latices of varying concentration. Estimates obtained in this way are shown in rows 3-4 of Table IV. Now it is unlikely that the thermal expansivity of latex of  $d_{29}^{29} = 1$  would be as low as water, or that that of latex of  $d_{29}^{29} = 0.96$  would be as great as pure rubber. Therefore, pending confirmation, Hartjens' figures must be rejected, on the ground that they show an unreasonably high value for  $d^2 S' / (dt dx)$ , that is, rate of change with varying rubber content ( $x$ ) of rate of change of density with temperature. (Possibly the data have been affected by observation of latices diluted with water to varying degrees, a practice which, according to de Vries, seems to have been common at the time of these observations.)

As an alternative method to obtain some estimate of the variation of specific gravity of latex with temperature, consider latex as a mixture of serum and rubber. By differentiating equations (2), (4) or (5)<sup>48</sup> with respect to  $t$ , we obtain the rate of change of the specific gravity of latex with temperature in terms of the rates of change for rubber and serum. Since we have observed that the specific gravity of the rubber phase in latex is equal to that of solid rubber, we may assume, as a working hypothesis, that its thermal expansivity is also equal. Unfortunately we have no data on expansivity of serum; presumably it is slightly greater than that of water, so as a first approximation consider  $dS_s'/dt \cong -d\rho/dt$ . Estimates of  $dS_L/dt$  obtained by this method are given in rows 5 and 6 of Table IV. They agree quite well with the values derived from Hartjens' data for  $S_L = 0.98$  to 0.99 (in which range most of Hartjens' observations were probably taken), and are rather more reasonable outside this range. We have therefore adopted these as the best estimates at present obtainable.

TABLE IV

ESTIMATES OF THERMAL VARIATION PER ° C OF THE SPECIFIC GRAVITY OF LATEX AROUND 29° C

## 1. Estimates from Hartjens' data for hydrometer corrections.

For latex having $S_{29}^{29} =$	1.00	0.99	0.98	0.97
(H) $-\delta u_t/\delta t$	0.26	0.34	0.42	$0.50 \times 10^{-3}$
(Ha) $-\delta S_4^t/\delta t$	0.29	0.36	0.44	$0.52 \times 10^{-3}$
(Hb) $-\delta S_4^t/\delta t$	(-0.01)	0.07	0.15	$0.24 \times 10^{-3}$

2. Estimates from  $dS'/dt$  of water and of rubber.

$S_{29}^{29}$ as above, d.r.c. =	17.9	26.3	34.8	43.6 per cent
(18b) $-dS_4^t/dt$	$\geq 0.37$	0.40	0.43	$0.46 \times 10^{-3}$
(18c) $-dS_4^t/dt$	$\geq 0.07$	0.11	0.14	$0.17 \times 10^{-3}$

Notes: In this table and in the following notes we use  $S$  with temperature affixes to indicate specific gravity, in place of the standard  $d_t^t$  to avoid confusion with the  $d$  of differentials.

Hartjens' data for hydrometer corrections conform to the formula:

$$(S_t' - u_t) = (0.00826 - 0.008 S_t') (t' - t) \quad (\text{H})$$

where  $t$ , the graduation temperature of the hydrometer, is about 29 to 31° C for instruments used by Hartjens and de Vries. From this we deduce:

$$(S_t' - S_4^t) = (0.00823 - 0.00794 S_t') (t' - t) \quad (\text{Ha})$$

$$(S_t' - S_4^t) = (0.00826 - 0.00827 S_t') (t' - t) \quad (\text{Hb})$$

The general formulas for the thermal coefficient of specific gravity of latex, related to those for serum and rubber phase, are:

$$\frac{dS_L'}{dt} = \frac{s^2 dr/dt - r^2 ds/dt}{rs(s-r)} S_L' - \frac{sdr/dt - rds/dt}{rs(s-r)} S_L'^2 \quad (18)$$

$$\frac{dS_L}{dt} = \left\{ \frac{s^2 dr/dt - r^2 ds/dt}{rs(s-r)} - \frac{d\rho/dt}{\rho} \right\} S_L - \frac{sdr/dt - rds/dt}{rs(s-r)} \rho S_L^2 \quad (18a)$$

Where  $r$  and  $s$  are  $S_4^t$  for rubber and serum, respectively, i. e.,  $S_R'$  and  $S_S'$  of former notation. Substituting values for 29° C,

viz.,  $\rho = 0.99597$ ,  $r = 0.910\rho$ ,  $s = 1.022\rho$ ,

$dr/dt = -0.000623$ ,  $-ds/dt \geq -d\rho/dt = 0.000295$ , the formulas used for estimating values in the above table are:

$$-dS_L'/dt_{29} \geq (0.00392 - 0.00356 S_L') S_L' = (0.00390 - 0.00353 S_L) S_L \quad (18b)$$

$$-dS_L/dt_{29} \geq (0.00362 - 0.00355 S_L) S_L \quad (18c)$$

Formulas directly in terms of d.r.c. can be most easily obtained by working with specific volumes and differentiating equations of the form of (5).

For variation of  $S_S$  and  $S_R$  with temperature of observation we have:

$$\frac{dS_R}{dt} = \frac{dS_R'/dt - S_R d\rho/dt}{\rho}$$

$$\frac{-dS_S}{dt} = \frac{(S_S - 1) d\rho/dt}{\rho}$$

whence, by substituting values for 28° C, we obtain expectations quoted on p. 488.

Throughout this paper I have dealt mainly with  $d_t^t$ , because that is the observation usually made in the East, and for which tables have been drawn up. The theory of the subject would, however, be appreciably simpler if we concerned ourselves only with density (or with  $d_4^t$ ), because the relative density of water ( $\rho$ ) would no longer require to be considered (compare Equations (1) and (3), or (18) and (18a)). Furthermore, temperature corrections for hydrometers (as distinguished from real changes in specific gravity) are smaller

for hydrometers graduated to indicate  $d_4^t$  than for those graduated  $d_t^t$ ; in practice the correction is often negligible (cf. Stott<sup>47</sup>). For many purposes it is also simpler to deal with specific volume than with specific weight (cf. Equation 5).

## ACKNOWLEDGMENT

I wish to express my thanks to Evan Guest for assistance with the writing of this paper, and to W. S. Davey for suggestions during revision. Ong Yoke Fong and Lee Yoke Heng have assisted with the computations.

## REFERENCES

- <sup>1</sup> Throughout this paper it is immaterial whether  $V$  be taken as  $1/S$  or as  $1/S'$ , provided, of course, that it be defined in the same way throughout any one equation. To avoid confusion, it should be noted that specific volume is usually defined as the mass of unit volume, and is equal to the reciprocal of density. It is, for most practical purposes, equal to  $V' = 1/S'$ , but differs from it in proportion as cc. differs from ml. By this definition it is not equal to  $1/S$ , but presumably it might be specifically so defined in a special context, as has been assumed by implication in the use of the term by van Gils (cf. *Arch. Rubbercultuur* **23**, 130 (1939)).
- <sup>2</sup> de Vries, "Estate Rubber", Batavia, 1920, 15, 56.
- <sup>3</sup> Rhodes, *India-Rubber J.* **39**, 397 (1935).
- <sup>4</sup> van Gils, *Arch. Rubbercultuur* **23**, 130 (1939).
- <sup>5</sup> A regression is a curve representing the relationship between two or more variates; it differs from equations of physics or of elementary mathematics in that it implies that observations may deviate from the curve for reasons other than mere experimental error; it is intended to represent the mean value of one (the dependent) variate for given values of the others. Readers unfamiliar with the term may, without serious error, replace it in this paper by "the equation representing the relationship between  $S$  and  $x$ ". The estimated regression coefficients are estimates of the constants (or parameters) of the equation.
- Standard errors may be interpreted as follows: If the true value of a parameter is  $\beta$  and our estimate of it (termed a "statistic") is  $b$ , the difference  $|b - \beta|$ , ignoring sign, has one chance in twenty (or a probability of .05) of being greater than twice the standard error. If we have two comparable statistics say  $b$  and  $b'$ , or a statistic  $b$  and a hypothetical value  $\beta$  which we think might be its true value, then  $P$  is the probability that  $|b - b'|$  or  $|b - \beta|$  might by chance be greater than the difference observed. Unless  $P$  is less than .05 it is not usually considered that we have obtained significant evidence against the hypothesis that  $b = b'$  (or  $\beta$ ).
- <sup>6</sup> Rhodes, *J. Rubber Res. Inst. Malaya* **5**, 234 (1934).
- <sup>7</sup> Since the only data now available are the 11 figures given in the published paper, these errors are determined from only 9 degrees of freedom and should be interpreted in conjunction with the table of  $t$  (Fisher, "Statistical Methods for Research Workers", Edinburgh, 1925-1935, 36). For  $n = 9$ ,  $t(.05) = 2.262$ ,  $t(.01) = 3.250$ . The 95 per cent confidence limits of  $Sx$ , as determined from these data, are therefore .9072 and .9122.
- <sup>8</sup> Bartlett, *J. Roy. Stat. Soc. Suppl.* **4**, 158 (1937).
- <sup>9</sup> See reference 7.
- <sup>10</sup> Deming, "Some Notes on Least Squares", U.S.D.A. Graduate School, Washington, 1938.
- <sup>11</sup> de Vries, *Arch. Rubbercultuur* **3**, 200 (1919) (Tables IV and V). Earlier data of de Vries and others appear to contain too many samples diluted with water to be of any use for our present purposes.
- <sup>12</sup> de Vries, *Arch. Rubbercultuur* **3**, 189, 204, errata (1919).
- <sup>13</sup> de Vries assumed that  $p$  was equal to unity, a not unreasonable approximation in these formulas. At 27-29° C  $Sx$  would be underestimated by about 0.0003,  $Ss$  would be overestimated by less than 0.00001.
- <sup>14</sup> Rhodes, *J. Rubber Res. Inst. Malaya* **9**, 126 (1939).
- <sup>15</sup> Furthermore, relative to the small range, experimental errors in observing d.r.c. may not here be negligible; by assuming so (see appendix 2) we may overestimate  $Sx$  and underestimate  $Ss$ .
- <sup>16</sup> Scholz and Klotz, *Kautschuk* **7**, 142 (1931).
- <sup>17</sup> Scholz and Klotz, *Kautschuk* **7**, 66 (1931).
- <sup>18</sup> Stamberger and Schmidt, *Rec. Intern. Rubber Congr., Paris, 1937*, 42; *RUBBER CHEM. TECH.* **11**, 479 (1938).
- <sup>19</sup> The diagram published by the authors does not correctly represent the data given in their Table I.
- <sup>20</sup> Bekkedahl, *J. Res. Natl. Bur. Standards* **13**, 411 (1934); *RUBBER CHEM. TECH.* **8**, 5 (1935).
- <sup>21</sup> Selected by Wood (*RUBBER CHEM. TECH.* **12**, 130 (1939)) as probably the most reliable observations of their class. Purification was by digestion with water at about 190° C, followed by extraction with water and with alcohol, and drying in an atmosphere of inert gas.
- <sup>22</sup> McPherson, *Bur. Standards J. Research* **6**, 751 (1932); *RUBBER CHEM. TECH.* **5**, 523 (1932).
- <sup>23</sup> By mischance van Gils' paper did not come to my attention until this paper was going to press; the paper by de Vries (*India-Rubber J.* **98**, 422 (1939)) was received still later. Consequently the bulk of this section was written after the rest of the paper was already in type. Van Gils gives data for the original ammoniated samples of latex from which the concentrates were derived, but the regression of specific volume on d.r.c. may be suspected of curvature (concave downward,  $P$  about 0.06—omitting sample no. 97, whose deviation from the regression is nearly seven times the standard deviation of a single observation). Consequently it is doubtful if the estimate of  $Sx$ , viz., 0.9067, by the method of section on Rhodes' data is valid. Ignoring the possible curvature and fitting the reciprocal of equation (6) (again omitting sample 97) we obtain:

$$VLM = 0.9777 + 0.1274 \frac{x_m}{\pm .00172 \pm .00474}$$

which may be compared with the corresponding equation derived from Rhodes' data, viz.:

$$V_{LM} = 0.9806 + 0.1283 x_m \\ \pm .00087 \quad \pm .00225$$

Having regard to differences in the ammoniation of the two groups of latex, these equations are in good agreement. The difference in slope is  $0.0051 \pm .0052$ , where  $0.00014$  is to be expected; the difference in ordinate at the mean d.r.c. (37 per cent) is  $0.0010 \pm .00027$ , where  $0.00091$  is to be expected. We may assume therefore that van Gils' original samples of latex were similar to those observed in other work reviewed above.

I am grateful to the Director of Research at the Proefstation, West Java, for information on the method of ammoniation used by van Gils, viz., 20 ml. of 20 per cent "ammonia liquid" per liter of fresh latex.

<sup>34</sup> de Vries, *India-Rubber J.* **98**, 422 (1939).

<sup>35</sup> de Vries, *India-Rubber J.* **89**, 343 (1935).

<sup>36</sup> de Vries, *Arch. Rubbercultuur* **3**, 183-206 (1919).

<sup>37</sup> In a recent paper, de Vries<sup>34</sup> renews his suggestion<sup>25</sup> that the rubber content determined after coagulation with acid in the usual way may be called "crepe rubber". However, as indicated in Section IV above, the term "crepe content" was originally put forward by Scholz and Klotz<sup>37</sup> to specify a d.r.c. determined after unusually thorough washing of the coagulum, assumed to be somewhat analogous to the extra washing received by crepe as opposed to sheet rubber. In my opinion the term should be restricted to the sense intended by these authors, consequently throughout this paper I have used "crude rubber" to indicate the mixture observed in ordinary routine work.

<sup>38</sup> Wood, *Proc. Rubber Tech. Conf., London 1938*, 938; *RUBBER CHEM. TECH.* **12**, 130 (1939).

<sup>39</sup> de Vries, *Arch. Rubbercultuur* **10**, 18 (1926).

<sup>40</sup> The amount of gas required to produce a given per cent by weight would vary with the specific gravity of the latex. The variation is however negligible, the error thus introduced into estimates of  $SLM$  over a range of 20 per cent d.r.c. being only of the order of 0.00005.

<sup>41</sup> de Vries, *Arch. Rubbercultuur* **1**, 242 (1917).

<sup>42</sup> Hartjens, *Arch. Rubbercultuur* **2**, 261 (1918).

<sup>43</sup> Rutgers and Maas, *Arch. Rubbercultuur* **1**, 289 (1917).

<sup>44</sup> de Vries, *Arch. Rubbercultuur* **1**, 246 (1917).

<sup>45</sup> de Vries, *Arch. Rubbercultuur* **1**, 247 (1917).

<sup>46</sup> Stott, "Hydrometers", in "Dictionary of Applied Physics", III, 431, London, 1923.

<sup>47</sup> de Vries, *Arch. Rubbercultuur* **1**, 248 (1917).

<sup>48</sup> de Vries, *Arch. Rubbercultuur* **3**, 189, 204 (1919).

<sup>49</sup> "International Critical Tables", III, 59 (1928).

<sup>50</sup> The temperature conditions are however indicated at only two places and the description of hydrometers as "densimeters" might mislead a casual reader, on referring only to individual sections, to assume that specific gravity means  $d_4^4$ , whereas in fact no determination of density is ever intended and all references are to  $d_4^t$ .

<sup>51</sup> Stevens and Stevens, *India-Rubber J.* **89**, 400 (1935).

<sup>52</sup> If we were to derive from Rhodes' data a table showing the relation between d.r.c. and the specific gravity appropriate for conversion to weight per gallon at 62° F, the resulting figures would differ from Rhodes' table by more than does the R.T.A. table. For example, for 35 per cent d.r.c. the R.T.A. table gives specific gravity 0.977, and Rhodes' table gives  $d_{20}^{20} = 0.9772$  from which we would estimate  $d_{62F}^{62F} = 0.979$  (or 0.980 for latex ammoniated with gas). Satisfactory figures for R.T.A. purposes can however only be derived from observations of latex as received in England.

Much of the comparison of different sets of data has centered around estimates of  $SR$  derived from them. But, since correct estimation of  $SR$  by extrapolation of a regression depends on knowledge of the quantity and specific gravity of admixtures in the observed latices, it is useless to estimate this character from an empirical table based on observations for which such conditions are unknown.

<sup>53</sup> Vernet, *Caoutchouc et gutta-percha 1910*, 4549.

<sup>54</sup> That is rate of change of the coefficient of expansivity with varying temperature.

<sup>55</sup> Dawson and Porritt, "Rubber: Physical and Chemical Properties", Croydon, 1935, p. 6.

<sup>56</sup> Data behind Hartjens' table have not (so far as I can discover) been published, but they appear to be a revision of observations exemplified by de Vries (*Arch. Rubbercultuur* **1**, 246 (1917)). The method of deriving average corrections for varying sp. grav. (or d.r.c.) is not stated.

<sup>57</sup> Stott, "Hydrometers", in "Dictionary of Applied Physics", III, 435, London, 1923.

<sup>58</sup> Equations (2), (4) or (5) are here more convenient than (1) and (3) because, for a given latex, d.r.c. per cent by weight is constant independent of temperature, whereas d.r.c. expressed as weight per volume is not independent of temperature. This is a point which seems to be not generally appreciated. The variation is not large, but for some purposes is appreciable. For example, latex of 50 per cent d.r.c. by weight would have about 4,800 lbs. per gal. at 29° C and 4,831 lbs. per gal. at 15° C (or 47.94 and 48.25 g. per 100 ml., respectively).



# ANALYSIS OF PROTEINS PRESENT IN HEVEA LATEX \*

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## INTRODUCTION

Very little in general is known about the proteins which are present in latex<sup>1</sup>, and research on the chemical composition of these substances and of their decomposition products (amino acids) is even scarcer, only two publications<sup>2</sup> being devoted to this subject.

The usefulness of a systematic investigation of this subject is obvious if the important part played by proteins in latex and also in coagulated rubber is borne in mind<sup>3</sup>.

It is well known that rubber, when coagulated by conventional methods, retains a considerable fraction of the proteins originally present in the latex. It is these proteins which occur in sheet and crepe rubber, and from which they can be separated only with difficulty<sup>4</sup>. The other proteins, *viz.*, those which remain dissolved in the serum, are therefore of no importance in connection with crude rubber; but they do influence the general qualities of the latex. Our investigation is limited to an analysis of these latter proteins.

For this purpose we employed the method described by Brazier<sup>5</sup>, which is based on differences in solubility of the copper salts of amino acids in water and in methanol. Although there are several methods for the analysis of proteins<sup>6</sup>, we chose this method, even if still not well known, because, according to Brazier, it gives excellent results. Furthermore, it seemed to us important to test Brazier's findings, particularly because, with the exception of a single publication, there are no data on the subject in the literature.

For the purpose of orientation, we began our investigation with an application of Brazier's method in its original form, which is also shown diagrammatically<sup>8</sup>, to make it clearer. We shall revert later to the preparation and the composition of the original product containing the proteins to be analyzed.

On the basis of the results obtained with Brazier's method, we are in a position to call attention to certain difficulties arising from the following circumstances:

1. Only eleven of the twenty-two amino acids isolated with certainty from the proteins could be separated with the aid of Brazier's method.
2. Conducting an air current through the barium hydroxide solution of amino acids led to decomposition of the various amino acids.
3. Alternating additions of sulfuric acid and barium hydroxide at the proper time during the entire analysis do not increase the effectiveness of the method, partly because the precipitated barium sulfate is difficult to refilter (filtration is possible only after heating on a water bath for a considerable time), and partly because the precipitate absorbs considerable quantities of amino acid, thus always leading to losses.
4. The differences in solubility of the copper salts of amino acids in water and in methanol are more or less arbitrary. This is especially true of those

\* Translated by A. H. Krappe for RUBBER CHEMISTRY AND TECHNOLOGY from the *Archief voor de Rubbercultuur*, Vol. 23, No. 4, pages 239-255, April 1939.



amino acids, the copper salts of which have different solubilities from those of the *l*-, *d*-, or *dl*-forms. We refer in this connection with the table on p. 20 of Klein's handbook<sup>5</sup> (cf. also under (7)).

5. The use of water on the one hand and of methanol on the other hand as solvents is not particularly convenient because anhydrous methanol, especially in a humid tropical atmosphere, absorbs water too easily, thus leading to the formation of methanol-water mixtures, the solvent power of which is between that of methanol and that of water. The results obtained with such mixtures are therefore obvious. At any rate, Brazier's instructions, according to which the copper salts are extracted ten times with anhydrous alcohol in an agitator, until "three successive extracts have the same weak blue color", is at least unsuitable for the tropics. Brazier himself remarked: "The methyl alcohol extract never becomes quite colorless, as some moisture is absorbed from the air."

6. As we found out ourselves, tyrosine is separated not only at the point indicated by Brazier (in the above scheme) but, in addition, at four other places, *viz.*, (a) in the glutamine fraction; (b) in the concentration of the solution of free amino acids obtained from the copper salts soluble in methyl alcohol; (c) in the proline fraction, and (d) in the valine fraction. The isolation of tyrosine at (b), (c) and (d) may be the consequence of incompletely dry methyl alcohol (cf. under (5)); the fact is that the separation of the amino acids in the glutamic acid fraction must take place. For it is known that the barium salt of tyrosine is not very soluble in water and still less so in dilute alcohol.

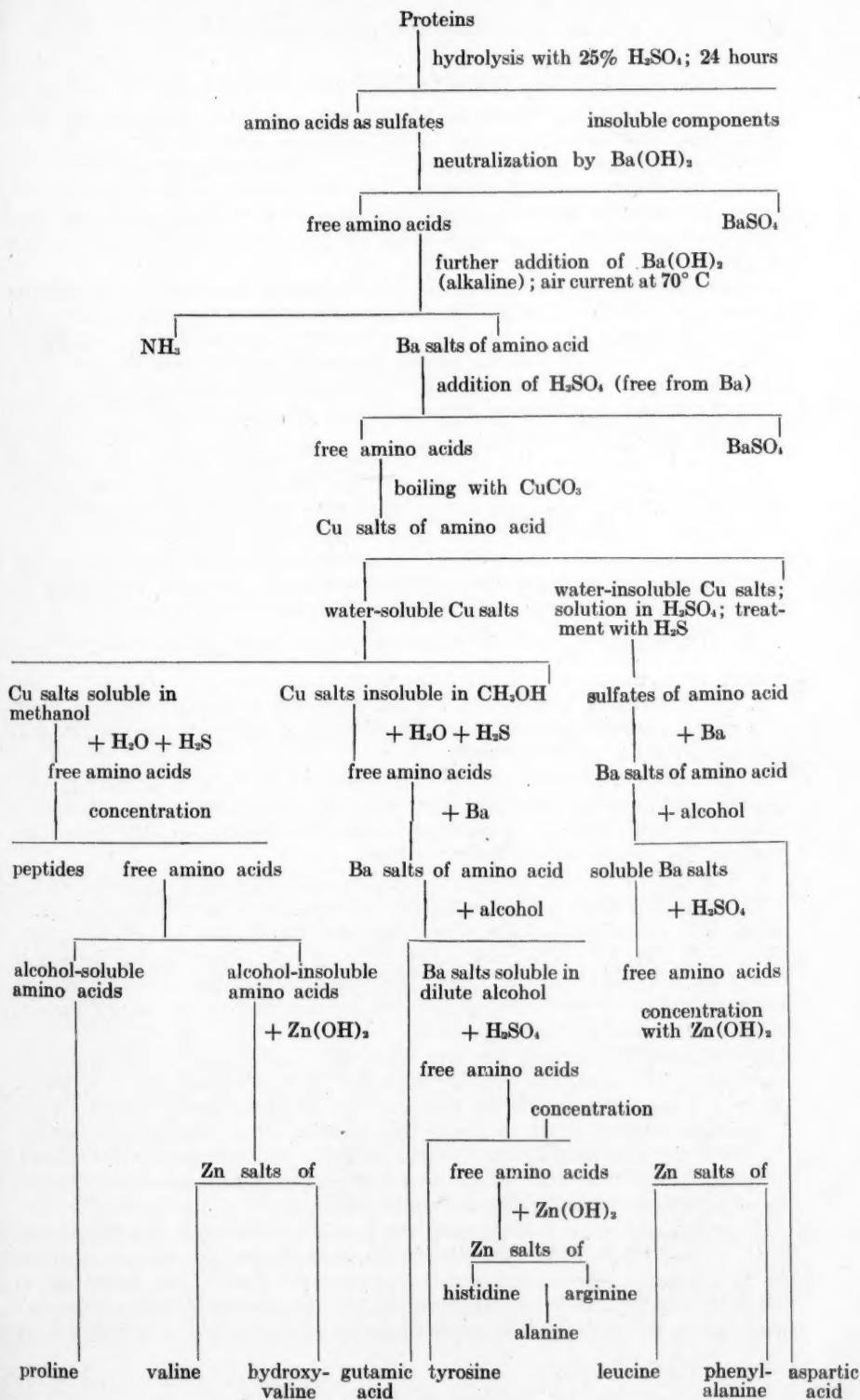
7. Finally attention should be called to the fact that we isolated leucine in large quantities in the arginine-alanine fraction. This is connected with the property of leucine to form mixed crystals with isoleucine and valine, both in the form of free amino acids and of their copper salts. These mixed crystals are much more easily soluble in the various solvents than are the special amino acids. If, for example, the solubility of leucine-copper in cold water is very small (1:3000), it becomes considerably greater in the presence of valine copper and (or) isoleucine copper (cf. also under (4)). In the application of Brazier's method, such surprises must therefore be expected.

These and other difficulties induced us to look for a possible improvement of Brazier's method. The facts listed under (1), (2) and (4) are hardly susceptible of modification. The difficulties mentioned under (3) may be partly overcome by the use of equally strong (equivalent) solutions of sulfuric acid and barium hydroxide, whereby it becomes possible to remove barium and sulfate from the solutions in question in a much shorter time. Furthermore, the turbidity of the solution containing barium sulfate when it runs through is a handicap, but may be prevented by boiling the solution with a little Norit<sup>10</sup> after the usual heating on a water bath.

As for the water absorption of methanol (cf. under (5)), it may be reduced to a minimum by continuous extraction of the copper salts in a Mann dialyzer. The Soxhlet apparatus for hot extraction is unsuitable for this purpose. However, the apparatus of Köhler is satisfactory, since its extraction chamber makes possible easy cooling from the outside.

To obviate the drawback mentioned under (7), it is useful to extract the mixture of the copper salts of amino acids first with methanol, then with water. By this means valine-copper and isoleucine-copper, both soluble in methanol, are separated from leucine-copper, which is insoluble in methanol. Once freed from the copper salts of valine and isoleucine, leucine-copper is soluble in water only with difficulty, and the free leucine can thus be isolated at the point indicated by Brazier. For the rest, we refer to the account of our observations as given below.

# SCHEME OF BRAZIER'S PROTEIN ANALYSIS



## SEPARATION OF PROTEINS FROM RUBBER SERUM

The composition and the content of protein remaining in the serum after coagulation of the rubber depend on the coagulant used, on the hydrogen ion concentration in the medium, and on other conditions directly connected with the type of *Hevea* tree from which the latex was obtained, and therefore necessarily vary more or less. For this reason we point out some peculiarities with reference to obtaining serum from which the proteins to be analyzed are precipitated.

Garden latex (31 per cent total solids) obtained in the Tjiomas experimental garden was diluted with water (90 l. of latex:67.5 l. of water), and was treated with dilute formic acid (1:50) (90 cc. of dilute formic acid per l. of diluted latex). After coagulation of the rubber, the serum remaining in the containers was worked up, together with the serum liberated during milling.

Of this serum, the following properties were determined:

1. The pH, which averaged 4.1;
2. Before determining the protein content, 2 liters of serum was saturated with chemically pure silver ammonium sulfate, allowed to stand overnight and then drawn off from the separated protein. After drying at 75° C, 7.572 grams of a product containing many impurities in the form of ammonium sulfate were obtained which, made homogeneous in a mortar, contained 59.4 per cent of this inorganic salt. As a result, the precipitated mixture contained more than 40 per cent of proteins and perhaps other precipitated substances, so that, in 2 liters of serum,  $\frac{40}{100} \times 7.572$  grams of proteins are present. The protein content thus amounted to about 0.15 per cent;
3. If the serum is treated with a base, an intense violet-blue color appeared at a pH of about 10.5, which, after the addition of still more base or an acid, disappeared again spontaneously<sup>10</sup>;
4. By boiling the serum, no more than one-third of the total amount of proteins present was precipitated; separation of proteins by means of sodium chloride seemed equally complete and was considerably smaller than that produced by means of ammonium sulfate;
5. Exposed to the air, the serum began to spoil only after the third day.

We worked up 220 liters of serum for this purpose. This quantity was saturated, in a galvanized iron drum provided with two faucets and with a gauge glass, with 150 kg. of technical ammonium sulfate. After rapid stirring, it was allowed to stand for 24 hours. The larger part of the separated protein was precipitated at the bottom of the vat; another part floated on the surface, with much foam and other impurities.

By means of the faucets, care was taken that only the part rich in proteins was caught in a decanting vat, in which the proteins were again precipitated after 24 hours. The volume of the concentrated protein suspension thus obtained amounted to about 35 liters. The proteins were then freed by suction with the aid of a battery of Büchner funnels. After drying at 75° C, the brown-gray hard mass was reduced to a fine powder in an iron mortar, strained through strainer 20, and made homogeneous.

A total of more than 1250 grams of this powder, which we shall call the crude product, was obtained. To determine its approximate protein content, 25 grams of the substance were treated with 1 liter of 2 per cent sodium hydroxide, in which the crude product was largely dissolved. Most of the soluble components were drawn off, and the light brown solution thus obtained was dialyzed for

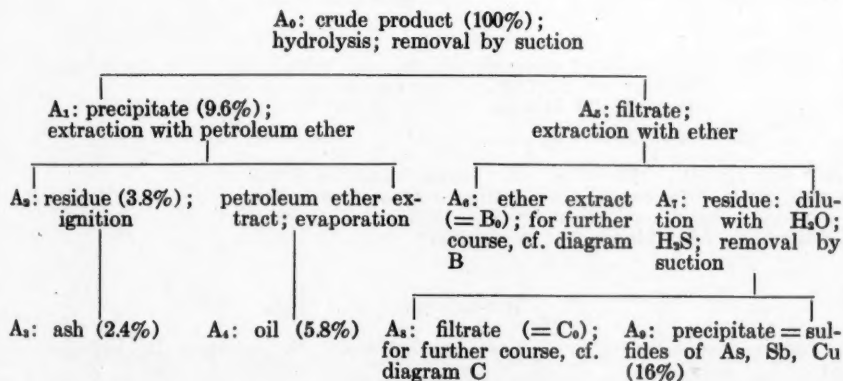
some time. After evaporating the dialyzed solution, nearly 10 grams of impure proteins was obtained, with ash<sup>11</sup> and moisture contents of 32.6 and 18.6 per cent respectively, so that the protein content of the crude product was about 20 per cent. We may add that the content of ammonium sulfate and other sulfates was about 50 per cent, while about 10 per cent of the crude product did not dissolve in 2 per cent sodium hydroxide. This insoluble part, on closer examination, seemed to contain fibers, sand and similar impurities.

#### PREPARATION OF A MIXTURE OF FREE AMINO ACIDS FROM THE SEPARATED CRUDE PRODUCT

By the addition of water, proteins may be split up into their components, amino acids. This hydrolytic cleavage, as is well known, may be brought about by means of enzymes, acids or bases. Following the example of Brazier, we used sulfuric acid. After some trials it seem to us, however, that the concentration of 25 per cent prescribed by Brazier was insufficient to complete the hydrolysis; better results were obtained with 33 per cent sulfuric acid.

Besides the desired amino acids, the crude product apparently contained various other substances, separation of which was included in our investigation (cf. Schemes A and B).

##### SCHEME A



Starting from 312.5 grams of crude product, i. e., a quantity containing about 62.5 grams of proteins, we obtained, after boiling<sup>12</sup> with 750 cc. of 33 per cent sulfuric acid for 24 hours, a dark brown solution containing impurities in the form of many solid particles. After cooling, it was drawn off.

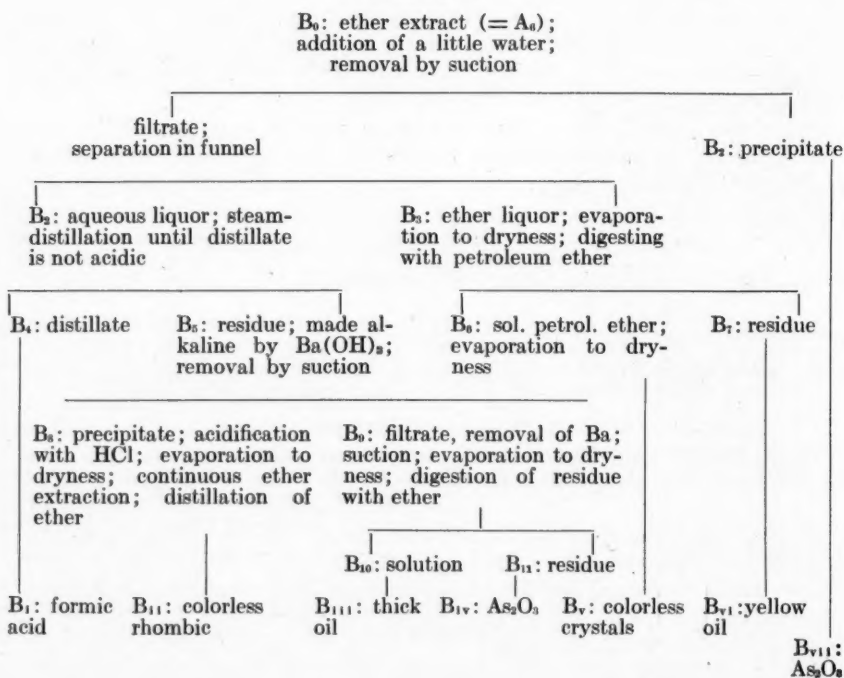
The precipitate (A<sub>1</sub>), after drying at 75° C and after extraction with petroleum ether in a Soxhlet apparatus for 12 hours, yielded an extract containing oil, and a residue (A<sub>2</sub>). The residue had a dry weight of approximately 11.9 grams and, after heating, yielded a yellow-white ash (A<sub>3</sub>), which contained Si, Cu, Pb, Fe, Al, As, and traces of Mg. From the extract a lighter red-brown thick oil (A<sub>4</sub>) was obtained by distilling off the solvent (about 17 grams).

The filtrate (A<sub>5</sub>), comprising among other substances the amino acids in the form of sulfates, was an almost opaque dark brown liquid. This was extracted in a Kutscher and Steudel apparatus for 72 hours continuously by means of

ether. The analysis of the ether extract ( $A_6=B_0$ ) was carried out according to Scheme B. Hydrogen sulfide was then conducted through the residue ( $A_7$ ), after diluting with an equal volume of water, until no further precipitate was visible; then the solution was extracted.

The  $H_2S$  precipitate ( $A_8$ ), of a yellow or brown-yellow color, weighed, after removal by suction and drying, more than 50 grams. It consisted largely of  $As_2S_3$  (96%), with approximately 2% of  $Sb_2S_3$  and 1.5% of  $CuS$ . These large quantities of arsenic to all appearances originate in the technical ammonium sulfate used. However, arsenic may also be separated from the ether extract  $A_6$  in the form of  $As_2O_3$  (cf. Scheme B).

## SCHEME B



This ether extract was not a homogeneous liquid, and at the bottom of the flask a yellowish semi-solid substance precipitated. At the same time the presence of a colorless crystalline substance was observed.

By addition of water, the semi-solid substance apparently went entirely into solution, while the glittering crystals ( $B_2$ ) remained nearly undissolved in water. The crystalline product was separated by suction; it apparently consisted entirely of  $As_2O_3$  (3 grams).

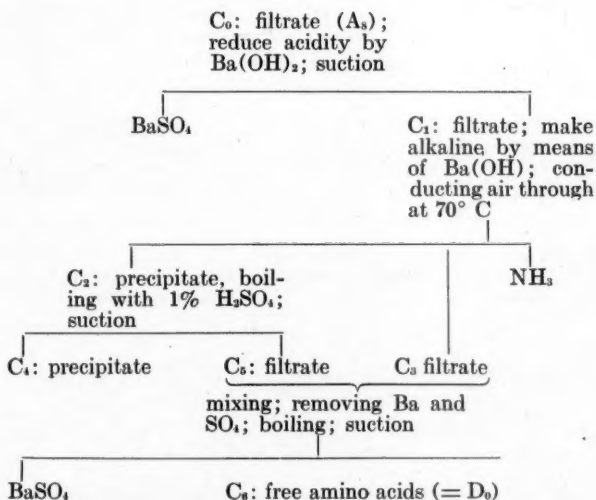
The rest of the procedure for analysis of the ether extract may be seen in the scheme. We shall revert to the substances  $B_{11}$ ,  $B_{13}$ ,  $B_{15}$ , and  $B_{16}$  in a later publication.

The main fraction  $A_8$  (cf. Schemes A and C) contained, besides amino acids, large quantities of sulfuric acid, ammonium sulfate, other soluble sulfates, mucous



substances and other organic impurities. From several preliminary tests it appeared that the directions of Brazier for the elimination of these admixtures are unsuitable. It is well to remove the larger part of the sulfuric acid and sulfates with enough barium hydroxide so that the mixture still shows, barely but distinctly, an acid reaction with Congo red. This prevents the retention of large quantities of amino acids still present in the mixture in the form of water-soluble sulfates by the precipitated barium sulfate. Washing the barium sulfate once with boiling water sufficed to bring the amino acids quantitatively into the filtrate ( $C_1$ ). This filtrate was a fairly light yellow liquid, and was only then made alkaline (pH approximately 12) by means of barium hydroxide, whereby barium sulfate and mucous substances were precipitated in the form of a gray sticky substance. Before removal by suction, air was conducted through the reaction mixture at 70° C until ammonia was no longer evolved.

## SCHEME C



The solution was drawn off, the filtrate  $C_3$  was set aside, the precipitate  $C_2$  was boiled with 1 liter of 1% sulfuric acid, and was drawn off again. The precipitate  $C_4$ , containing, besides barium sulfate, mucous substances, etc., referred to, was thrown away. The filtrate  $C_5$  was added to  $C_3$ , the mixture was completely freed from barium and sulfates, was heated quickly and was subjected to suction. The filtrate thus obtained ( $C_6$ ) contained the free amino acids in a fairly pure condition. By evaporating on a water bath and drying in a vacuum desiccator, a dark brown mixture of the free amino acids was obtained, which probably still contained impurities in the form of water-soluble inorganic salts and organic compounds, such as sugars, aliphatic carboxylic acids, etc. It was possible to eliminate these impurities completely by the soda-alkaline solution of the amino acid mixture in the conventional manner<sup>9</sup>, and treatment with a solution of mercury acetate, after which the precipitated mercury salts of carbamic acid are again transformed into amino acids by means of hydrogen sulfide. A total of 43.0 grams of these purified amino acids was obtained, *i. e.*, 13.8 per cent of the crude product.

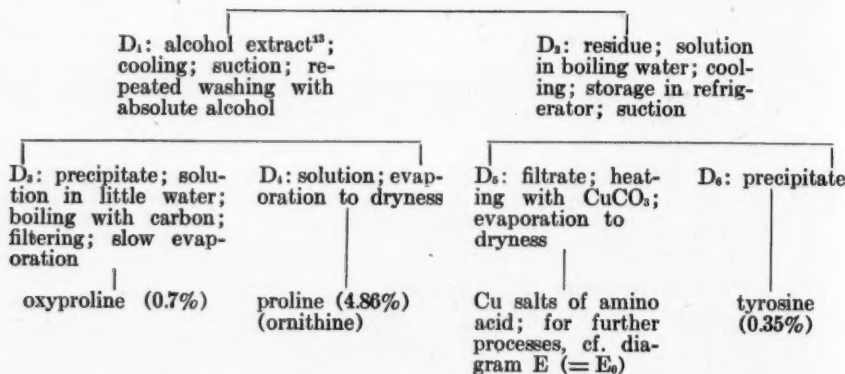
## ANALYSIS OF THE MIXTURE OF AMINO ACIDS

As has been pointed out, we obtain less favorable results by the original method of Brazier. This was particularly true of the separation of tyrosine and leucine. It is also very difficult to keep anhydrous methanol water-free, and the mixture from which the copper salts of amino acids are to be extracted contains considerable quantities of proline-copper, which is particularly hygroscopic; as a result methanol becomes even more unsatisfactory.

In looking for possible improvements, we were guided by the fact that tyrosine is soluble in water only with difficulty, while proline is the only amino acid easily soluble in ethanol. These properties were taken advantage of (bearing in mind certain precautionary measures, about which see below) to extract the mixture before transformation of the copper salts.

## SCHEME D

D<sub>0</sub>: dry mixture of amino acids (13.8%);  
continuous extraction with absolute  
alcohol for 2 × 24 hours



After a number of preliminary experiments, we finally arrived at the following systematic method of analysis, which yielded satisfactory results.

The finely powdered brown mixture of amino acids was dried by heating in a dry chamber at 110° C for one hour and storage in a vacuum desiccator over phosphorus pentoxide. The powder thus obtained, which must be perfectly dry, was then put through the process described in Scheme D.

Here it is well to point out the following facts. It is necessary to make the alcohol perfectly water-free before use. Samples with absolute alcohol prepared in the conventional manner confirmed the general fact that, besides proline and oxyproline, still other amino acids (leucine, valine, etc.) were extracted. This is natural enough if it is remembered that ordinary absolute alcohol always contains 0.2-0.5 per cent of water. These small quantities of water may be completely eliminated by following the directions of Smith<sup>14</sup>. Extraction, which it is advisable to carry out cold, is best done in the dialyzer of Mann mentioned above.

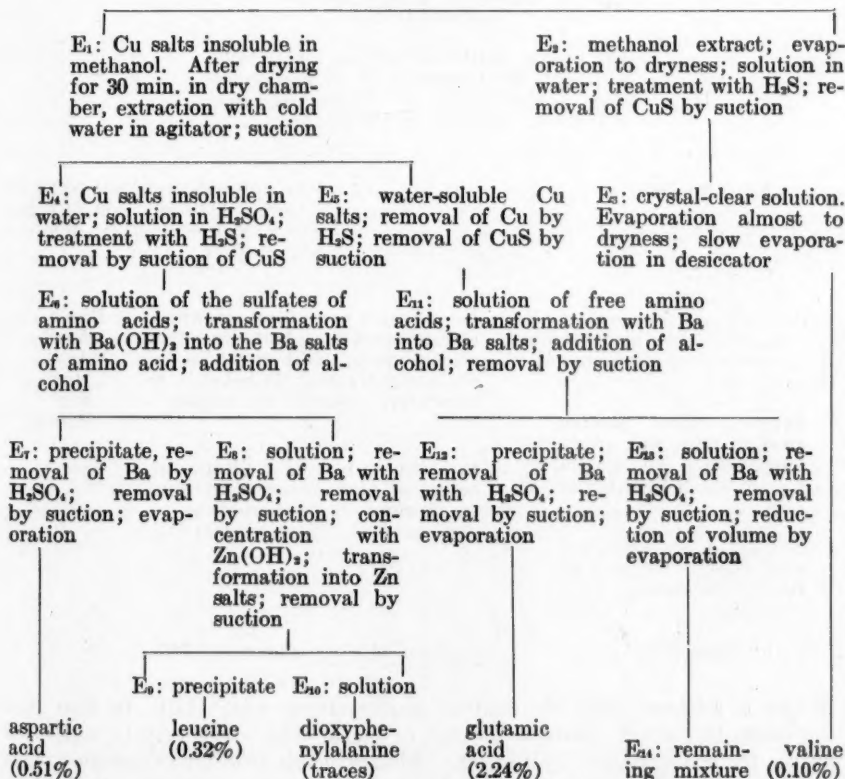
Crude proline, which appeared to contain ornithine was, when dried in a desiccator, a brown, very hygroscopic, amorphous-solid substance. Of oxyproline,

which is a crystalline white substance, 2.2 grams were separated. We shall revert to the purification of these and other separated amino acids in a later study.

The tyrosine which was separated was fairly pure. It was obtained by boiling residue  $D_2$  with water until all went into solution. Then the lighter solution was allowed to stand for 24 hours or longer in a refrigerator, and the precipitate was filtered and recrystallized in as little water as possible. The

## SCHEME E

$E_0$ : dry powder of copper salts of amino acid; continuous extraction with methanol



mother liquor was evaporated, and the residue was digested with ice water. After filtering, the ice-water extract was added to the extract  $D_5$  obtained previously. The part which remained insoluble was likewise tyrosine, which with the main part weighed 1.1 grams.

The transformation of the remaining amino acids into copper salts was accomplished easily by boiling the filtrate  $D_5$  with enough  $CuCO_3$  until carbon dioxide was no longer evolved. Then about 50 grams of  $CuCO_3$  was added, and the mixture was evaporated to dryness on a water bath. This process was re-

peated twice. The light blue amorphous substance, obtained by drying in an oven at 110° for several hours and cooling in a vacuum desiccator over sulfuric acid, was a fine powder.

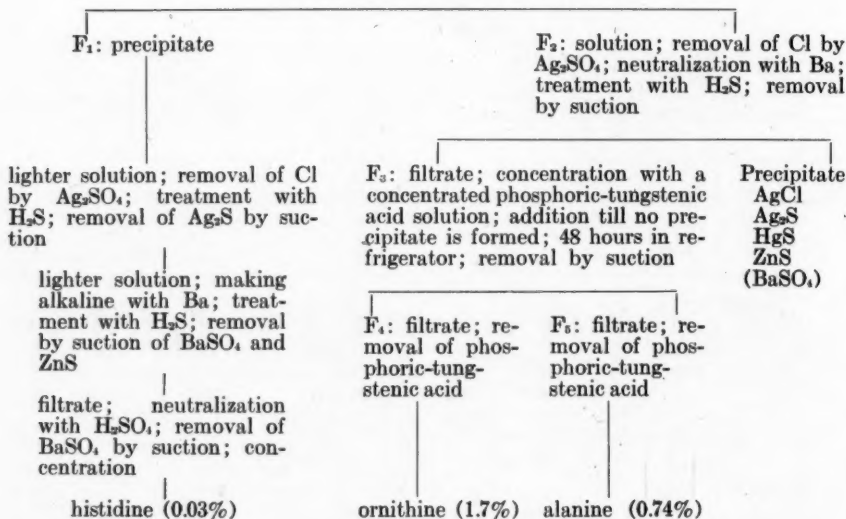
Scheme E indicates the next steps in the investigation.

It is advantageous to extract the dry powder of the copper salts of the amino acids (contrary to the directions of Brazier) first with methanol, which can be carried out best in the dialyzer designed by Mann, and which is continued until the methanol extract is perfectly colorless. As for the other processes indicated in the scheme, we refer to the publication of Brazier for details.

Here the following observations may be useful. It may happen that in the case of incomplete extraction with anhydrous ethanol (diagram D) not all

#### SCHEME F

F<sub>0</sub>: residue mixture; boiling for 30 min. with Zn(OH)<sub>2</sub>; removal by suction; addition of HgCl<sub>2</sub> solution till no precipitate is formed; removal by suction

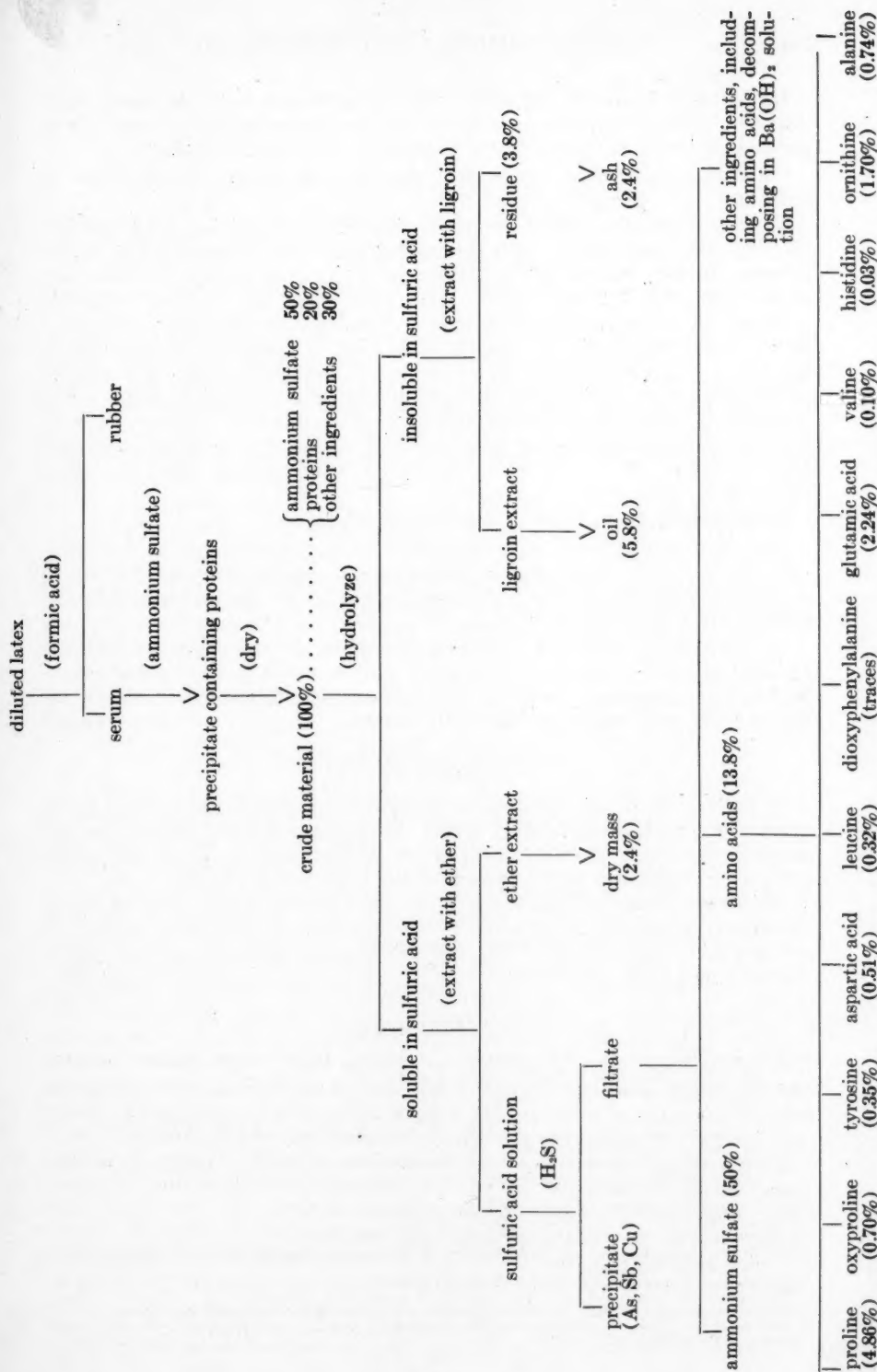


proline is removed from the mixture of dry amino acids (D<sub>0</sub>). In that case the valine fraction E<sub>3</sub> contains the rest of the proline, which may be separated by the method indicated by Brazier. This also holds true for oxyproline. This phenomenon, which in itself is not decidedly disturbing, may be entirely prevented by continuous extraction with alcohol for at least 48 hours.

Above all, in the separation of glutamic acid, it must be remembered that this compound may only too easily be transformed into  $\alpha'$ -pyrrolidone- $\alpha$ -carboxylic acid (pyroglutamic acid).

Fortunately, the reaction is reversible, and closing of the ring may be prevented by boiling the reaction product, which is a mixture of glutamic acid and pyroglutamic acid, and cannot be crystallized, with 2 N HCl for several hours. A solution of the hydrochloric salt of glutamic acid is obtained, and, after evaporation on a water bath, this is easily crystallizable.

SCHEME G





In the residual mixture ( $E_{14}=F_0$ ), which still remains to be examined, there may be present (according to Brazier) histidine, arginine and alanine. These amino acids can be separated by the method set forth in Scheme F<sup>5</sup>.

Of crude histidine only a very small quantity, viz., barely 100 mg., could be separated.

The dry substance obtained by evaporating filtrate F<sub>2</sub> weighed approximately 7.5 grams, and no arginine could be detected in it. This compound was apparently completely transformed, in the course of the analysis, into ornithine. As is well known, this transformation takes place easily in a barium hydroxide medium. In all probability, the process mentioned in Scheme C ( $C_1 \rightarrow C_8$ ) may be held responsible for the transformation in question. It must be remembered that we continued the air supply in the barium hydroxide solution of the amino acids much longer than did Brazier, since we had to decompose a considerable quantity of ammonium sulfate. This seemingly explains the fact that, contrary to Brazier, we were unable to obtain any unchanged arginine. However that may be, ornithine was separated as a nearly white crystalline substance in the amount of 5.2 grams.

Of nearly pure alanine, we obtained about 2.3 grams.

The procedure indicated in Scheme F is time-consuming, but it does yield satisfactory results, since only the elimination of chlorine from the solution in question requires full attention. A small trace of hydrogen chloride inhibits the crystallization of ornithine.

All amino acids separated in the manner described above can be identified by their physical constants and chemical properties. In a later study we intend to return to this subject, and at the same time shall describe the preparation of other products which have been isolated.

### SUMMARY

To analyze the proteins present in rubber-free serum obtained by coagulating latex for the preparation of sheet rubber, the method described by Brazier<sup>5</sup> was adopted. Inasmuch as this method is not wholly satisfactory, particularly in the humid atmosphere of the tropics, it was improved in several ways.

Besides several amino acids, some interesting byproducts were isolated, among others a yellow-reddish thick oil, and other ether-soluble substances. Scheme G outlines the results attained. The properties of the products isolated will be discussed in a later publication.

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- <sup>4</sup> "Science of Rubber" (Memmler), edited by Dunbrook and Morris, New York, 1934, 170; "Chemistry and Technology of Rubber", edited by Davis and Blake, New York, 1937, 91, 251.
- <sup>5</sup> Brazier, *Biochem. J.* **1930**, 1188.
- <sup>6</sup> Klein, "Handbuch der Pflanzenanalyse", Vienna, 1933, Part IV, 1-180.
- <sup>7</sup> Kögl and Erxleben, *Z. physiol. Chem.* **258**, 57 (1939).
- <sup>8</sup> Block, "Determination of Amino Acids", Minneapolis, 1938, 75.
- <sup>9</sup> Norit is an activated carbon obtained from organic material in steam at 500° C; cf. Winkler Prins, "Algemeene Encyclopaedie".
- <sup>10</sup> Belgrave and Bishop, *Malayan Agr. J.* **11**, 271 (1923).
- <sup>11</sup> This ash was of a brick-red color, and was rich in arsenic and antimony.
- <sup>12</sup> To prevent excessive foaming, several cc. of octyl alcohol was added to the reaction mixture.
- <sup>13</sup> Analysis of this alcoholic extract is far from completed; it is hoped to return to this subject later.
- <sup>14</sup> Smith, *J. Chem. Soc.* **1927**, 1288.

# HEVEA LATEX SLUDGE

## EXISTENCE OF A SLUDGE FRACTION IN FRESH UNPRESERVED LATEX \*

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Bruce<sup>1</sup> recorded the results of analyses of the ash of certain crude rubbers, among them of evaporated latex. He found the sample investigated to contain 5.8 per cent MgO and 24 per cent  $P_2O_5$ . It is evident that ammoniation of a latex containing such ions would result in the formation of insoluble  $MgNH_4PO_4 \cdot 6H_2O$ .

Hauser<sup>2</sup> refers to this phenomenon, stating that the precipitated salt settles to the bottom of the container. This precipitate, sometimes containing occluded rubber, has been known in the plantation industry as latex sludge, and has constituted a fouling problem in storage containers.

The presence of a sludge fraction in fresh unammoniated latex, just as it is produced by the tree, has not been generally recognized. Van Harpen<sup>2</sup> concentrated fresh unpreserved latex by centrifuging and, on opening the centrifuge, observed a sludge deposit in the bowl. He records that this sludge darkened rapidly and states that it was rubber-free and friable.

As a beginning in a study of latex desludging procedures in this laboratory, a quantity of the sludge was obtained and analyzed. The data obtained are reported here.

### EXPERIMENTAL PROCEDURE

A quantity of fresh latex was obtained by 7 A.M. on the day of tapping, immediately diluted with an equal volume of distilled water, and then passed twice through the clarifying bowl of a laboratory Sharples supercentrifuge, operating at about 40,000 r.p.m. A considerable volume of sludge was obtained on the first passage and only a trace on the second, which showed that practically all of the sediment which was removable at this centrifuging speed had been removed. This sludge was immediately suspended in distilled water, the suspension centrifuged, and the process repeated in order to wash out any latex remaining in the sludge. Inasmuch as the diluted latex had a density of about 0.98, it was possible that a portion of the sludge could have remained in the wash water if it had had a density slightly below 1.00. To prove this, the washings were treated with 1 per cent of a proprietary emulsifying agent, sold under the name of Emulphor O, and then made up to contain 20 per cent by volume of ethyl alcohol. The density of such a solution is near that of the latex, and the Emulphor O has been found by experiment to prevent coagulation of the small amount of latex rubber in the washings when alcohol is added, but not to prevent sedimentation of such sludge. This mixture was recentrifuged, but only a trace of sludge was obtained; thus the major portion of this fresh latex sludge has a density greater than that of distilled water, since it sediments out almost entirely if a water suspension is centrifuged.

A portion of the wet sludge was dried 8 hours in an oven at 100° C to constant weight. The dry material was slightly elastic but very "short", and resembled

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 3, pages 439-440, March 1940.

highly compounded rubber. Each granule was covered by an oily film, and the surface of the dish in which it was dried was oily. The material was found to be sufficiently rubbery so that it would cohere if milled with the rolls set not too close together.

Another portion was evaporated nearly to dryness at room temperature *in vacuo* over sulfuric acid. This portion had a bad odor when removed, indicating bacterial or enzymic action.

A third portion was treated while wet with three separate quantities of re-distilled acetone, filtered, and dried *in vacuo* over sulfuric acid. The acetone washings were dried on the steam bath, and the acid number of the residue was obtained.

From ash, nitrogen, acetone-extract, and carbon tetrachloride-extract analyses of the first and last portions described above, the composition of this sludge appears to be as shown in Table I.

TABLE I  
COMPOSITION OF SLUDGE FROM FRESH UNPRESERVED LATEX

Moisture in wet sludge.....	83.5 %
Dry sludge in undiluted latex.....	0.11
Dry sludge in latex total solids.....	0.27
1. Acetone ext. of dry sludge.....	29.5%
2. Rubber content of dry sludge <sup>a</sup> .....	36.0
3. N in extd. residue, based on original dry sludge.....	3.44
4. N in ext., based on original dry sludge.....	0.63
5. Protein equivalent to No. 3 (% N $\times$ 6.25).....	21.5
6. Ash in extd. residue, based on original dry sludge....	1.5
7. Ash in ext., based on original dry sludge.....	2.5
Total .....	91.0

<sup>a</sup> Obtained by extracting the acetone-extracted sludge with carbon tetrachloride.

The 9 per cent unaccounted for represents error in the analyses, possible error in the use of the factor of 6.25 for calculating the protein content from the nitrogen content, water lost by dehydration of inorganic bodies during ashing, and possibly a small amount of an unidentified substance.

Of the acetone extract, 20.6 per cent was present in the acetone washings of the original wet sludge. This was quite oily and had an acid value of 71.25, equivalent to a free acid content, calculated as stearic, of 36.13 per cent. The remaining 8.9 per cent was removed slowly by acetone extraction in a Soxhlet type of extractor, and had an acid value of 4.8. This latter portion of the extract was a yellow, waxy semisolid resembling the *Hevea* lipin described by Rhodes and Bishop<sup>4</sup>. It should be noted that *Hevea* lipin prepared in this laboratory was found to have an acid value of 2.3, whereas Rhodes and Bishop reported a value of 14.

The fresh wet sludge is rapidly dispersible in dilute ammonia or other alkalis to yield a permanent suspension, from which only traces of sediment can be removed by even long-continued and exhaustive centrifugation. The residue after acetone and carbon tetrachloride extraction is only slightly dispersible in dilute ammonia solution, but is sufficiently so to give a strong biuret test for protein.

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# NEW TYPES OF TRANSFORMATION PRODUCTS OF RUBBER \*

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In the present paper, a few observations are described which were made in the last few months by Philipp and one of the present authors (Posnansky).

When a solution of silver nitrate in a mixture of acetone and water, which is a satisfactory solvent for silver nitrate and at the same time has a sufficiently strong swelling action, is allowed to react with crude rubber in the form of films prepared from latex, products are obtained whose properties depend on the concentration of the solution, on the time of reaction and on the temperature, and differ fundamentally from the properties of the original rubber. When highly purified latex is used for preparing the films, the already familiar reducing action of rubber on silver nitrate does not take place, and colorless or white films are obtained, within which considerable quantities of inorganic substances are embedded. Determinations of the silver contents of these products showed values up to 18 per cent of silver, corresponding to approximately 37 per cent of silver nitrate, the actual percentage depending on the time that the reaction was allowed to continue. That a very strong addition reaction takes place becomes evident, for example, by the fact that when a similar latex film is swollen in a silver perchlorate solution of the same concentration, only 2.5 per cent of silver, *i. e.*, less than one-seventh as much as with silver nitrate, was found in the end product, which, moreover, gave no indication that any fundamental changes had taken place, such as are described below for the reaction between rubber and silver nitrate.

The product obtained from the reaction of rubber and silver nitrate was a compact, leathery film, which had lost the softness and tackiness of the original latex film. The specific gravity of 0.923 of the original latex film increased to 1.25 in the case of the product containing approximately 18 per cent silver.

When this product was examined by x-rays, the diffuse ring characteristic of unstretched rubber was not in evidence but, instead, a series of sharp rings which did not resemble either the rings of frozen (crystallized) rubber or those of the silver compounds in question. When the film was stretched, the x-ray diagram changed, without any noticeable change in the glancing angle, into a sharply defined fibre diagram which was different from that of ordinary stretched rubber. When the rubber film was irradiated parallel to its plane, a different x-ray diagram was obtained; from this it is evident that when the product is stretched an orientation higher than that of a fibre structure is formed, as is the case with ordinary rubber.

Furthermore, the product differed from ordinary rubber in some of its other physical properties. Its high resistance to tearing was particularly surprising, in fact it was 15 to 20 times as great as the resistance of the original film, and was superior to the tear resistance of vulcanizates of high quality. Also, the tensile properties of the product were such that only at very high stresses

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Atti del X Congresso Internazionale di Chimica*, Roma, May 15-21, 1938, Vol. 4, pages 98-99. This paper is considerably more detailed than an earlier one on the same subject by Kratky, Philipp, Posnansky and Schossberger (cf. RUBBER CHEMISTRY AND TECHNOLOGY 11, 661 (1938)).

was there any considerable elongation, and after reaching a certain critical elongation, additional stress increased the elongation only slightly. Finally at a very high stress, the product split as a fibrous structure, and then ruptured.

Evidence in the x-ray diagram of a fibrous structure appeared slowly as the steep section of the stress-strain curve was reached, and the fibrous structure became more clearly defined only at the highest elongations. This corresponded to a very high stress, which was many times greater than the stress necessary to bring out a fibre structure in ordinary rubber.

When the stress was released at room temperature, the greater part of the elongation was retained and, correspondingly, the fibre diagram in the x-ray diagram remained wholly unchanged when the stress was released, even after standing for one month at room temperature after release of the stress. Only at relatively high temperatures, *i. e.*, between 95° and 110° C, did the product retract and its fibre structure disappear. However, even at these temperatures, and also at slightly higher temperatures, fusion took place, with partial decomposition of the product and change to a brown color because of separation of colloidal silver. When the product was heated to still higher temperatures, it decomposed, with foaming and, when it was incinerated on glass, a silver mirror remained.

Attempts to prepare corresponding products by the use of solutions of other metal salts have so far been unsuccessful. With gold chloride, silver perchlorate and sodium nitrate, the x-ray diagram of rubber remained unchanged, or at most the interferences were complicated by the diagrams of the metals or their salts. Evidence of a crystal diagram in the unstretched state at room temperature has so far been limited to the silver nitrate-addition product of rubber.

The minimum proportion of silver nitrate consumed which is necessary to bring about the changes described has not yet been determined. It varies within wide limits, so that, for example, a product containing approximately 12 per cent of silver and a product containing approximately 18 per cent of silver (corresponding to approximately 20 and 37 per cent, respectively, of the silver nitrate consumed) showed nearly the same properties from the point of view described above.



# RUBBERLIKE PROPERTIES OF POLYBUTENE \*

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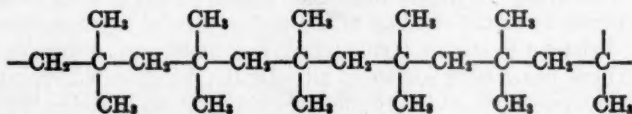
Until the last decade the explanation of those properties for which rubber is unique was confined largely to the study of rubber itself. Duplication of these properties involved the synthesis of polymers from isoprene and its immediate homologs.

The discovery that chloroprene could be polymerized to a rubberlike substance altered the character of the study and represented a distinct departure in the type of diolefin used. The production of Thiokol, phosphonitrile, and the various vinyl polymers has resulted in the duplication of certain rubberlike physical properties by chemical structures wholly unrelated to rubber. Observation of the behavior of these newer elastics must lead to the conclusion that many physical characteristics of rubber are not inherent in the conformation of the rubber molecule alone. Whitby suggested that any general view of the structure of rubber can be regarded as acceptable only if it is applicable to other elastic colloids<sup>21</sup>. Conversely, those properties of rubber which are not shared by other elastics must be explained by structural features not common to them all.

A logical product to consider for the segregation of properties relating to the rubber structure per se and those capable of being shared by other molecules is hydorrubber<sup>18</sup>. This substance has been observed to have certain "rubbery" properties, but unfortunately for comparison it has been prepared only in a degraded or low molecular weight form and therefore (from the standpoint of physical state) is not directly comparable with rubber.

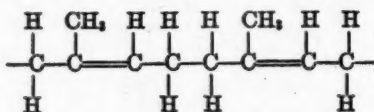
On the other hand, the recently developed butene polymers are available over a wide molecular weight range<sup>10</sup>, those of medium or high molecular weight, i. e., from 30,000 to 300,000, closely resembling rubber in the following respects: (a) they are essentially pure hydrocarbons; (b) they are long molecules; (c) they have a regular distribution of short aliphatic side substituents.

The most characteristic chemical difference between the polybutenes and rubber is that rubber has a plurality of unsaturated linkages amounting to approximately one double bond per 5-carbon unit, whereas from iodine numbers and theoretical considerations, the butene polymers are saturated except for one theoretical terminal double bond. In the case of the polymers of higher molecular weight where isobutene is by far the predominating constituent unit, the evidence points to long chains of the following chemical structure:



\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 5, pages 731-736, May 1940.

For comparison, the generally accepted structure of rubber is given as:



A comparison of these polymers, with respect to properties common to both, leads to certain interesting conclusions concerning those properties of rubber for which unsaturation alone is responsible.

#### MECHANICAL TREATMENT

Mechanical working as produced by a rubber mill or a Banbury mixer causes a degradation in the molecular weight of polybutene. This breakdown is not so rapid as it is for rubber, although as in the case of rubber, it is more pronounced at lower temperatures.

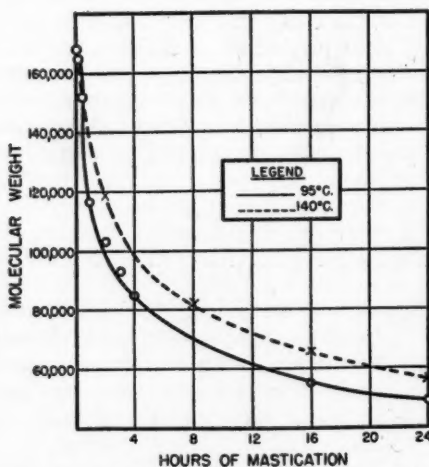


FIG. 1.—Molecular weight degradation vs. time of Banbury mastication.

The rate of breakdown of 168,000 molecular weight polybutene was determined by milling in a laboratory Banbury mixer at two different temperatures—95° and 140° C (203° and 284° F). The former temperature was maintained by circulating cold water through the jacket of the mixer, and the latter by circulating steam. These breakdown data are shown graphically in Figure 1.

#### BEHAVIOR IN SOLVENTS

The polybutenes are miscible in all proportions with aliphatic hydrocarbon solvents. Dissolving the higher molecular weight polymers is more difficult and is characterized by initial swelling of the mass, followed by formation of viscous solutions. Behavior in other solvents is largely a function of molecular weight, the lower polymers being more soluble in all solvents; for example, dioxane dissolves only very low polymers, and ethylene dichloride will not dissolve the solid intermediate polymers, whereas hot benzene dissolves all but the very high polymers.

The behavior of medium molecular weight polybutene in ethylene dichloride is reminiscent of the action of rubber in ethyl ether. The two phenomena may not be strictly analogous, but the diverse character of data on the quantitative occurrence of sol and gel forms of rubber using different solvents, and the peculiar character of sol rubber itself in solution as observed by Staudinger<sup>16</sup> indicate the importance of molecular weight in this phenomenon. If, as Staudinger contended and as the data on polybutenes indicate, selective solubility is primarily a function of molecular weight, the early efforts of Hauser and others to ascribe the general elastic behavior of rubber to its heterogeneous action towards solvents appear to require some modification. This view is in accord with that of Whitby<sup>21</sup>, who believes that rubber does not consist of rubber hydrocarbon in merely two states of polymerization, but is a mixture of an unbroken series of polymers representing a rather wide range of degrees of polymerization.

Data on the distribution of the various molecular weight fractions of polybutene are shown in Figure 2. This curve was obtained by careful precipitation

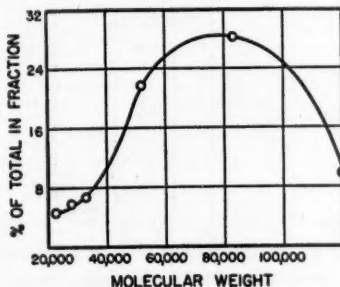


FIG. 2.—Precipitation of 60,000 molecular weight polybutene from diisobutene solution by isopropyl alcohol.

of 60,000-molecular weight polybutene from very dilute solutions in diisobutene by isopropyl alcohol.

The possible relation between thickening power in solution and other properties of polymeric substances was first suggested by Schidrowitz and Goldsborough<sup>13</sup>, who believed viscosity to be a measure of "inner properties" which determine the strength and nerve of rubber. In accordance with the Staudinger concept of macromolecules<sup>15</sup> and their behavior in solution, the thickening power of the polybutenes has been used as a measure of their respective molecular weights, as described in another paper<sup>20</sup>. In subsequent discussions it will be understood that the term "molecular weight" refers to measurements obtained by this procedure.

Additional data presented here will show that many properties of polybutenes are closely related to viscosity effects, whereas other properties appear to be independent of molecular weight.

#### VULCANIZATION

Polybutenes of either high or low molecular weight have not so far been vulcanized by any conventional rubber-curing technique, although experiments toward this end are being continued. Treatment of the low polymers with excess sulfur monochloride at elevated temperatures causes a change in solubility,

cold flow, etc., suggestive of the changes that take place when rubber is vulcanized. Large quantities of hydrogen chloride are evolved during this reaction<sup>19</sup>.

After the polymer is heated with sulfur and other conventional curing and compounding agents, it is still soluble in hydrocarbons; its extensibility has not been decreased or its elasticity increased, and the tensile strength, which is commonly used to measure degree of curing for rubber, does not change greatly. Continued heating brings about gradual degradation, so that prolonged vulcanizing temperatures will result in slightly lower tensile strength values. Since this degradation or depolymerization is inhibited by the presence of sulfur, an ordinary vulcanization mix will degrade more slowly than pure polybutene.

Mixes containing even very high percentages of sulfur, of accelerators, or of both, exhibit none of the common manifestations of vulcanization. Four formulas, which are among the many tried, are shown below. The polybutene

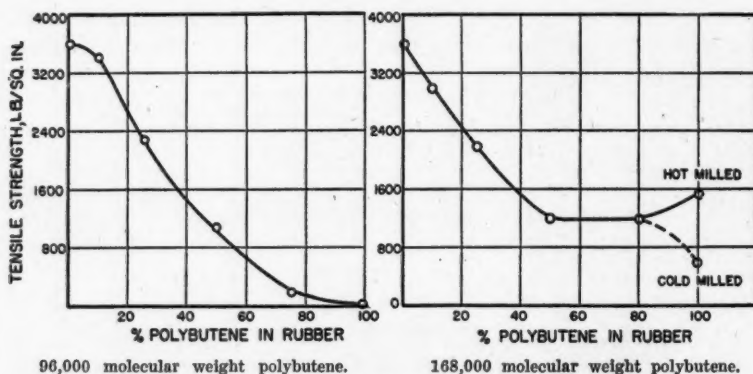


FIG. 3.—Tensile strength of vulcanized rubber-polybutene compounds.

was mixed with these ingredients on the rubber mill in the usual manner. The samples were placed in molds and pressed at 130° C (266° F) for 2 hours. For other samples, the temperature was increased to 155° C (311° F). Values for tensile strength, solubility, etc., taken after heat treatment, were about the same as for the original, and indicated that no measurable vulcanization had taken place. This is not surprising, since Staudinger and Fritzsche<sup>17</sup> showed that hydrorubber having appreciable unsaturation does not vulcanize in the conventional manner:

Formula No.	1	2	3	4
Polybutene (168,000 mol. wt.)	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	3	3	3	3
Sulfur	10	1	1	3
Tetramethylthiuram disulfide (Tuads)	—	1	—	3
Butyl Zimate	2	—	—	—
Diphenylguanidine (D. P. G.)	1	—	—	—

#### TENSILE STRENGTH AND ELONGATION

The tensile strength and elongation of polybutene depend largely on the molecular weight of the polymer. As would be expected from analogy with vinyl polymers, the higher the molecular weight, the greater the tensile strength. Since butene polymers ranging in molecular weight from 112 to 400,000 can

be prepared, it follows that tensile strength will vary accordingly. However, as Figure 2 shows, polybutenes of high molecular weight are composed of a series of polymers of different molecular weight, some higher and some lower than the numerical value determined by viscosity measurement. This is also true of rubber<sup>21</sup>.

Polymers below 80,000 in molecular weight have low tensile strength, but when the molecular weight is increased to 150,000 or more, the tensile strength may readily be determined by means of a standard Scott tester.

Important in this connection is the treatment imposed on the polybutene before pressing in a hot mold into the form of a tensile sheet. If polybutene of high molecular weight is worked on a cold open mill for about 5 minutes, or until it forms a sheet which can be molded, such a slab is much lower in strength than the same material which has been masticated in a hot Banbury mixer for about 20 minutes before pressing in the mold. As an example, polybutene of 168,000 molecular weight was worked on a cold open mill for 5 minutes. This polymer, which then had a molecular weight of 148,500 due to breakdown, was pressed in a tensile slab mold for 15 minutes at 141° C (285.8° F). The tensile strength was 540 pounds per square inch. For comparison, a similar piece of the same polybutene was milled at 140° C (284° F) in a midget Banbury mixer for 20 minutes. After this treatment the polymer was quickly sheeted out on an open mill, then pressed into a sheet under the same conditions as was the first stock. At the end of the sheeting operation the tensile strength of the polybutene was 1510 pounds per square inch.

In another example, approximately 200,000 molecular weight polybutene was used and the same procedure was followed. The tensile strength, in pounds per square inch, was as shown below:

5 min., cold open mill mixing.....	680
20 min., Banbury milling (140° C).....	1900

In view of these results, it might almost be said that a kind of mechanical vulcanization had taken place. This may be brought about by aligning and compacting the molecular chains more closely against each other so that greater intermolecular forces are brought into play. This is reversible, since polybutene which has been treated to give a high tensile strength will, when again milled cold, revert to its original low tensile strength characteristics. Other examples of fiber orientation have been observed in the case of polystyrene<sup>21</sup> in the familiar instance of racked rubber and in the polyamide fibers recently developed by Carothers<sup>2</sup>.

This phenomenon of mechanically increased tensile strength is not manifested by mixtures of polybutene and rubber. The tables which follow list the tensile strength and elongation of various vulcanized rubber-polybutene stocks made in accordance with a standard procedure:

	Parts
Smoked sheet .....	100
Zinc oxide .....	5
Stearic acid .....	3
Sulfur .....	2
Tuads .....	0.75

The various percentages of polybutene were mixed with broken-down rubber on a laboratory rubber mill, and this mixture was compounded with the vulcanizing ingredients. The compounds were vulcanized in standard molds, 0.075 inch thick, in a steam-heated platen press for 15 minutes at 131° C (268° F), the optimum cure.



The results given in Table I are presented graphically in Figures 3 and 4. The stress-strain curves for these compositions indicate that in concentrations of polybutene below 50 per cent the ordinary rubber characteristics are evident. Beyond that point the polybutene characteristics come to the front; that is, the stress-strain curve is of a different shape, manifesting higher elongation at lower loads.

In rubber-polybutene mixtures the difference between high and medium molecular weight polymers is not evident as a function of tensile strength until

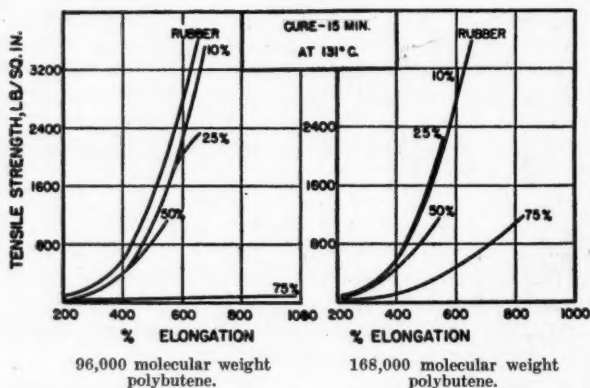


FIG. 4.—Stress-strain curves for rubber-polybutene vulcanizates containing 10 to 75 per cent polybutene.

TABLE I  
TENSILE STRENGTH OF RUBBER-POLYBUTENE MIXTURES

	Rubber	Polybutene in rubber mix					Cold-milled polybutene
		10%	25%	50%	75%	100%	
		96,000 MOL. WT. POLYBUTENE					
Tensile (lbs. per sq. in.).....	3600	3500	2300	1100	200	—	—
Elongation (%) .....	650	675	650	550	975	—	—
168,000 MOL. WT. POLYBUTENE							
Tensile (lbs. per sq. in.).....	3600	3000	2200	1200	1200	1510	540
Elongation (%) .....	650	600	550	550	875	600	550

more than 50 per cent of the polymer is present. However, at 75 per cent the tensile strength advantage of the 168,000 molecular weight material is evident. (This critical concentration range is discussed further under "Behavior toward Ozone" and "Action of Acids".)

#### ELASTIC PROPERTIES

Since all matter is capable of deformation, the critical factor of elasticity is obviously retractability or tendency to revert to the original shape. The different manifestations of elasticity are expressed by terms such as elastic memory, elongation, snap, elastic limit, modulus, and racking. Of these, the last two are more closely identified with forces of distortion and are discussed under "Tensile Strength and Elongation".

Naunton arrived at a definition of "a rubber" based on degree of elongation and rate of retraction or snap in the temperature range in which rubber

exhibits these properties<sup>9</sup>. Acceptance of this view eliminates low molecular weight polybutenes from further discussion. In the molecular weight range of 27,000 to 30,000, however, the polybutenes acquire a state of decreased deformability rather rapidly and show high elongation accompanied by a mild degree of snap. With increase in molecular weight, the rate of retractability increases and the property of tensile strength assumes importance. Elongation is slightly reduced and a definite elastic limit becomes apparent. With the lower molecular weight polybutenes the permanent set is fairly high.

The higher polybutenes exhibit elastic memory to an undesirable degree, particularly when worked at low temperatures, as indicated by the tendency of the material to curl on removal from a cold or slightly warm mill. This tendency is largely overcome by maintenance at a high temperature (90° to 100° C or 194° to 212° F) for a short time.

The temperature range of elasticity of the higher polybutenes is remarkably wide. Sheets of the material do not become brittle at -78° C (-108.4° F) and, contrary to the behavior of most high polymers, they do not soften and melt together at high temperatures (180° C or 356° F) but actually appear to dis-aggregate or lose cohesion under milling at these temperatures.

It is apparent from the foregoing that the "super" polybutenes exhibit rubber-like elasticity to a remarkable degree. Since these polymers are saturated, with the exception of one theoretical terminal double bond, any concept of elasticity based on unsaturation must necessarily be excluded. This applies particularly to the spiral theories of Fikentscher and Mark<sup>3</sup>, Hauser and others, and to the theories based on the geometric isomerism of the rubber molecule of which a portion of the hydrogen evaporation theory of Mack<sup>8</sup> is an example.

Much of Mack's criticism of the views expressed by Staudinger and Leopold<sup>18</sup> that the elastic properties of hydorrubber are determined by molecular weight is obviously not applicable to polybutenes which have a high rate of retractability and tensile strength in the rubber range.

The various theories of entangled fiber structure present a pretty picture, but do not adequately explain reversible entanglement necessary for rapid retraction. Houwink<sup>7</sup> diplomatically suggested that the truth probably lies in a combination of the many theories suggested for explaining elastic properties. In accord with this view we propose simply that:

1. Tensile strength results from forces holding molecules together.
2. Long-range elasticity results from forces between different portions of individual molecules.

Elasticity and strength in the oriented condition are therefore caused by the equilibrium between intermolecular and intramolecular forces. The attraction of molecules for one another intermolecularly is generally accepted. The tendency of molecules to overcome the action of external molecular forces and to be attracted intramolecularly is illustrated by the work of Ruzicka<sup>11</sup>, who showed that large rings do not assume the uneven shape which would be expected from the play of distorting influences from adjacent molecules, but are actually collapsed rings occupying a space only two chain diameters in width and having a length approximately half the circumference of the chain:



Expected ring structure.



Found by Ruzicka.



FIG. 5.—Effect of exposure to ozonized air for 20 minutes on rubber compounded with varying proportions of polybutene.

Forces similar to those causing the collapse of large rings, *i. e.*, intramolecular, may well explain the reasons for reversible entanglement of very long molecules without assumption of the strain configuration attributed to the geometric form of rubber.

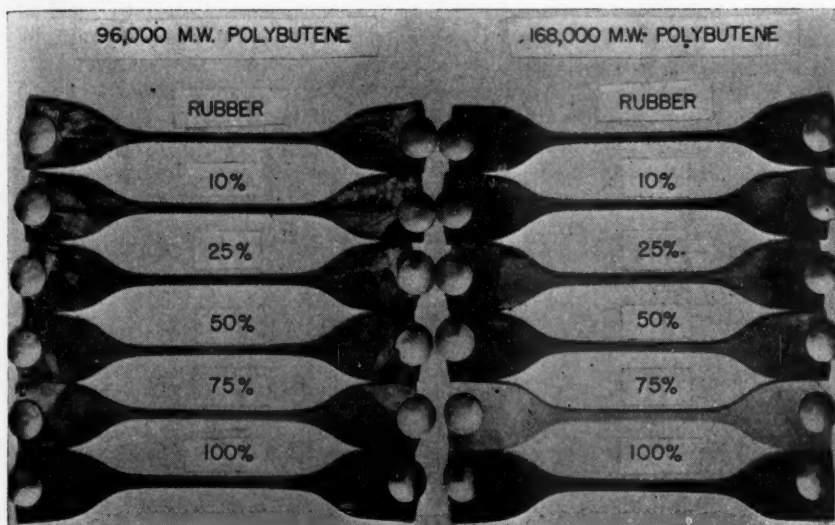


FIG. 6.—Effect of concentrated sulfuric acid on rubber compounded with varying proportions of polybutene.

#### BEHAVIOR TOWARD OZONE

Ozone is the prime destroyer of vulcanized rubber. Haushalter, Jones and Schade<sup>6</sup> showed that slightly stretched rubber in an atmosphere containing as little as 0.1 per cent ozone will crack almost instantly. It appears that stretching or straining, though ever so slight, greatly accelerates the action of ozone on rubber. This straining need not be greater than that produced by the bend in an ignition wire or the twist in a cable. It is indeed through the area of 5 to 10 per cent elongation that ozone cracking is most pronounced<sup>14</sup>; above this area the rubber cracks less readily.

The action of ozone is a kind of laceration of the rubber normal to the direction of mechanical strain. Its progress may be readily observed through the glass wall of an ozone-filled jar. As if invisible knives were cutting the rubber, small incisions appear immediately. These increase in number and depth until the sample breaks; they are not heterogeneously scattered or formally reticulated, but all are parallel with one another and normal to the line of strain.

As Harries<sup>4</sup> suggested, the action of ozone on rubber and other unsaturated compounds appears to be through the formation of ozonides at the double bonds. If this is true, it follows that saturated compounds such as polybutene would not be affected by ozone, or at least only slowly and probably by way of a different mechanism.

To test the resistance of polybutene to ozone cracking, strips of rubber, polybutene, and the rubber-polybutene mixtures used in the tensile strength tests were cut from tensile sheets into strips approximately 6 inches long and 0.5 inch wide. They were wound helically around glass tubes, fastened in position,

and placed in a desiccator through which air containing ozone was passing. As in the tensile strength tests, two polybutene compounds were used, one of 96,000 molecular weight, the other of 168,000 molecular weight. The results of this test are shown in Figure 5, taken after 20 minutes of ozone exposure.

The samples were visually examined at intervals and ratings given to designate the degree and progress of cracking. For this purpose an arbitrary scale of from 1 to 10 was used; 1 indicated incipient cracking and 10 complete rupture. The ratings are listed in Table II.

The rubber and rubber-polybutene mixtures which contained either 10 or 25 per cent of the synthetic polymer were ozone cut immediately. In the 50-50 mixtures cracking did not take place until 8 or 10 minutes after exposure.

TABLE II  
OZONE CRACKING OF RUBBER-POLYBUTENE MIXTURES

Min. of exposure	Pure gum rubber	Polybutene in rubber mixture				
		10%	25%	50%	75%	100%
168,000 MOL. WT. POLYBUTENE IN RUBBER						
1.....	5	5	3	None	None	None
5.....	7	7	5	None	None	None
10.....	9	9	9	None	None	None
20.....	9	9	9	None	None	None
96,000 MOL. WT. POLYBUTENE IN RUBBER						
1.....	5	5	3	None	None	None
5.....	7	7	7	None	None	None
10.....	9	9	9	4	None	None
20.....	9	9	9	8	None	None

#### ACTION OF ACIDS

Soft rubber vulcanizates are attacked rapidly by strong mineral acids at room temperature. Oxidizing acids such as nitric and sulfuric are quicker and more vigorous in their action than, for example, hydrochloric acid. Concentrated nitric acid dissolves vulcanized soft rubber almost completely and leaves as residue only the insoluble fillers and a small amount of hornlike substance. A yellow resin is precipitated on dilution of the acid.

The polybutenes are inert under these conditions, although hot concentrated nitric acid will produce a yellow, sticky, oxidized polymer after prolonged treatment.

What is true for ozone resistance is true also for acid resistance, in that the inert character of the polybutenes toward concentrated acids is conferred on rubber-polybutene mixtures when quantities approaching 50 per cent are used (Figure 6). The specimens were prepared by first immersing them in concentrated sulfuric acid for 5 minutes, then stretching them 25 per cent, and nailing them in that position. The rather critical concentration required indicates that the polybutene must be present in an almost continuous layer at the point of attack. Although the polybutene and crude rubber appear to be homogeneously miscible, the ultimate vulcanized product may be presumed to comprise a rubber-filled polybutene. If this is correct, a pure polybutene might be expected to be superior, but the great improvement in the ease of mechanical working on the mill, etc., of the broken-down rubber-polybutene mixture appears to counterbalance this advantage for many structural purposes.



## REBOUND

The bouncing properties of the polybutenes are considered apart from the discussion of elasticity because of the marked lack of correlation between these properties. Most of the theories concerning rebound of elastic materials have placed great weight on rate of retraction or, more precisely, since this is a compression phenomenon, on the rate of restitution of the body deformed by impact. In the case of rubber, such an assumption is unlikely, because highly broken-down plastic forms of rubber have rebound closely approximating that of the undegraded crude rubber or even, as shown by Williams<sup>22</sup>, that of soft vulcanized stocks. These degraded samples show practically no retraction on slow deformation. The rebound of rubber might be attributed to unsaturation and the concomitant kinking of spiral molecules, but this is disproved by the peculiar behavior of substantially saturated and highly degraded hydorrubber which bounces almost to the same extent as rubber itself.

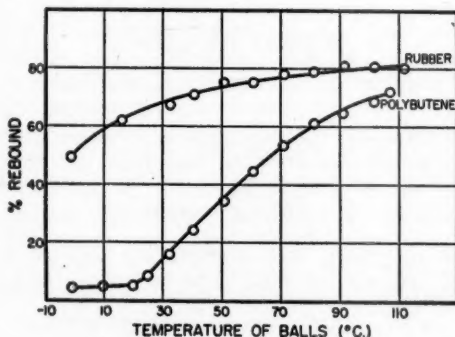


FIG. 7.—Rebound of 168,000 molecular weight polybutene balls and vulcanized pure gum rubber balls falling under their own weight from a height of 1 meter.

As measured by the percentage return of solid balls when dropped on a steel plate from a height of 1 meter (3.3 feet), the polybutenes show practically no rebound at ordinary temperatures, either in plastic, low molecular weight forms (where they resemble hydorrubber) or in the highly retractive, super-polymeric state (where they resemble tough crepe rubber).

However, the behavior of the polybutenes at higher temperatures is enlightening, since merely raising the temperature by 100° C produces rebound closely approaching that of rubber at the same temperature. Stated differently, the temperature of rebound and the temperature coefficient of rebound of the polybutenes are at marked variance with those of rubber (Figure 7).

On the other hand, Thiokol with poor elongation and retractive properties has an even flatter temperature curve of rebound than rubber, along with a rebound at 100° C equal to that of rubber and the polybutenes.

## ELECTRICAL PROPERTIES

Polybutenes have excellent electrical properties, as would be predicted from their saturated hydrocarbon structure. They show good resistance to moisture and to changes in electrical properties due to immersion<sup>12</sup>. Representative data

on 200,000-molecular weight polybutene are compared with those on smoked sheet rubber as follows:

	Temp., ° C.	Power factor	Dielectric constant	Breakdown volt- age, kv./mm.
Polybutene .....	20	0.0004	2.3	23
	85	0.0005	2.2	—
Rubber .....	25	0.0016	2.38	—

#### THERMAL DEGRADATION

Polybutenes, like rubber, can be thermally decomposed to lower hydrocarbon units. The degradation of rubber has been observed to yield as high as 25 per cent of the isoprene monomer. Polybutenes generally yield about 50 per cent of the original monomer on thermal degradation. Of the remaining products, about 25 per cent is dimer. The structure of the dimer has provided a basis for speculation on the structure of polybutene.

#### X-RAY PATTERNS

Brill and Halle<sup>1</sup> obtained x-ray diagrams of stretched polybutene which show a remarkable similarity in behavior to that of rubber, since in the stretched condition an excellent x-ray fiber diagram is obtained, whereas in the normal state it is roentgenographically amorphous.

#### ACKNOWLEDGMENT

The writers wish to express their appreciation and thanks to many of their associates who have coöperated with them at various times during the course of the experimental work.

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# CATALYTIC DEHYDROGENATION OF MONOÖLEFINS TO DIOLEFINS

## SOURCE MATERIALS FOR SYNTHETIC RUBBER AND RESINS \*

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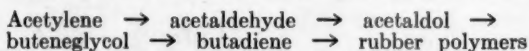
Aside from the scientific value of the method described here for the catalytic dehydrogenation of monoölefins to diolefins, the present contribution has an important industrial, commercial, and military value, *viz.*, as an economic source of raw material for synthetic rubber. The production of butenes from butanes and pentenes from pentanes has already been described<sup>8, 9</sup>.

The present paper, showing the production of butadiene from butenes and isoprene from pentenes, is the connecting link between the billions of cubic feet of butanes present in natural and cracked gases and of butenes present in the latter, and the billions of gallons of pentanes available in natural gasoline and crude oil on the one hand, and the production of synthetic rubber from these raw materials on the other.

The basic raw materials for the production of synthetic rubber therefore now include our tremendous resources of hydrocarbon oils, hydrocarbon gases, and coal to produce synthetic hydrocarbons, if and when our petroleum resources become exhausted.

The production of synthetic rubber from butadiene and isoprene is well known. Wallach<sup>12</sup> exposed isoprene to light and produced synthetic rubber. Matthews<sup>8</sup> and Harries<sup>5</sup> independently used metallic sodium to polymerize isoprene to rubber. Similar work has also been done by others.

So-called Buna rubbers<sup>7</sup>, made and used on a commercial scale in Germany, are polymers or mixed polymers of butadiene synthesized from acetone:



Most of the synthetic Buna rubber is not polymerized by sodium but is produced by emulsion polymerization. Also the commercial Buna rubbers are copolymers of butadiene with other materials.

Similar developments have taken place in Russia<sup>1</sup>, where ethyl alcohol is employed as a source of butadiene. However, as one of the authors pointed out<sup>9</sup>, "the development of the synthetic rubber industry depends upon the production of cheap butadiene and isoprene", and "catalytic dehydrogenation of butenes or pentenes or corresponding saturated hydrocarbons, butanes and pentanes, points the way to cheap production of butadiene and isoprene."

Another important development is the production of synthetic resins of the resin-rubber or rubber-resin type by the copolymerization of butadiene with another olefin, *e. g.*, styrene, the properties of the product depending on the relative proportions of the diolefin and monoölefin.

In the previous papers<sup>8, 9</sup> the catalytic dehydrogenation of gaseous paraffins to monoölefins was described. This process is not limited to the production of olefins from paraffins; the olefins can be further dehydrogenated with the same

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 3, pages 309-311, March 1940.

catalysts (chromium, molybdenum, or vanadium oxide on alumina<sup>3, 4, 9</sup>) to diolefins. The diolefins formed are of the conjugated type, and have the same carbon framework as the parent olefin.

Thus from 1- or 2-butene, 1,3-butadiene is formed; from straight-chain pentenes, piperylene (1,3-pentadiene); and from branched-chain pentenes, isoprene (2-methyl-1,3-butadiene). The original position of the double bond in the framework of the olefin is probably of no consequence since, especially in the presence of the alumina base catalyst, it is freely shifted<sup>6, 10</sup>. Thus isoprene was obtained in approximately equal yields from either 3-methyl-1-butene or from a mixture of 2-methyl-1-butene and 2-methyl-2-butene.

One conjugated diolefin (1,3-cyclopentadiene) was obtained in one operation from the corresponding saturated hydrocarbon cyclopentane.

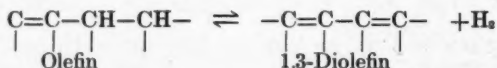
The single-pass formation of diolefins from saturated hydrocarbons is not limited to the cyclopentane ring system. In the dehydrogenation of *n*-butane to butenes, small percentages of 1,3-butadiene are produced, the amount depending on the conditions.

Olefins whose carbon frameworks do not permit the introduction of conjugated double bonds, *e. g.*, ethylene and propylene, gave, as the predominating reaction, hydrogen and carbon. No tendency to form acetylenes or diolefins of the allene type was observed. These observations also apply to the behavior of 1,3-butadiene in the presence of the dehydrogenation catalysts. In this latter case the formation of liquid polymerization or condensation products (about 5 per cent) was observed.

Single-pass yields of diolefins from monoolefins up to 20-30 per cent were obtained. In the vacuum dehydrogenation of butenes, recycle yields of the order of 60 to 79 per cent are possible.

#### CONDITIONS

The reaction with which we are chiefly concerned may be represented by the general equation:



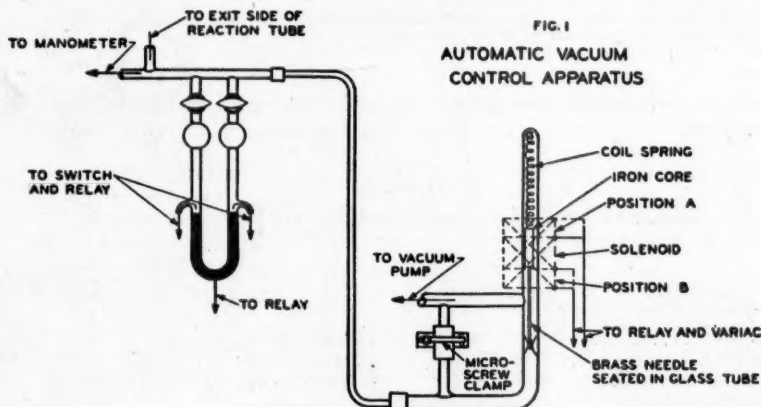
[This equilibrium for butene-butadiene was recently investigated by Dement'eva, Frost, and Serebryakova<sup>2</sup> in the range 480-534° C.] The olefin in the presence of hydrogen is also in equilibrium with the corresponding paraffin, but this reaction is negligible under the conditions of the present experiments. As is the case with the dehydrogenation of paraffins, the equilibrium of this reaction is shifted to the right with increase in temperature. Moreover, since the reaction to the right represents an increase in the number of moles, it is favored by decrease in pressure. In view of these considerations the reactions were performed at reduced pressure, *viz.*, 0.25 atmosphere and lower, and in most cases at a temperature of 600-650° C.

#### EXPERIMENTAL PROCEDURE

The dehydrogenations were carried out by passing the charge at a definite rate through a section of granular catalyst in a quartz tube. The catalyst zone was heated in the constant-temperature zone of an electrically heated aluminum-bronze block furnace. Condensable products were collected in solid carbon dioxide traps, and the noncondensable gases were pumped from the system by

means of a Nelson vacuum pump, which permitted metering and sampling for analysis.

The pressure was automatically controlled by a solenoid valve arrangement, the essentials of which are shown in Figure 1. The valve consists of a brass stem ground into a glass seat. An iron core is attached at the top of the brass stem. This is actuated by means of the solenoid when the circuit is completed in the proper arm of the mercury manometer (so constructed that either side may be used). One side of this manometer is left open to the system; the other is closed when the desired pressure is reached. The variety of adjustments of which the apparatus is capable makes it applicable to a wide range of pressures and space velocities. For example, the position of the solenoid can be adjusted so that the valve is opened when the circuit is completed (position A); or it can be adjusted so that the valve is held shut when the circuit is complete



(position B). If desired, a portion of the gas may be by-passed by adjusting the microscrew clamp.

The condensed reaction products were usually fractionated in a Podbielniak column, and the cuts investigated by chemical methods.

**Catalysts.** In general the catalysts were of the chromium, molybdenum, or vanadium oxide on alumina type, recently described<sup>3, 4, 9</sup>. The preparation of a laboratory chromium oxide on alumina catalyst was also given in detail<sup>4</sup>. The results described in the present paper were obtained with alumina impregnated with 4 per cent by weight of chromic oxide.

**Identification of Products.** The diolefins were identified by the preparation of crystalline derivatives, either the maleic anhydride addition compounds, the tetrabromides, or both (Table I). Butadiene was determined in vaporized samples by absorption in maleic anhydride<sup>11</sup>. This method was also adapted to the 5-carbon diolefins by vaporizing a weighed sample in sufficient nitrogen to keep it in the vapor phase.

## RESULTS

The yields of the diolefins under the conditions used are given in Table II. They do not necessarily represent the optimum conditions. To obtain the optimum, a series of experiments under different conditions was made with *n*-



TABLE I  
IDENTIFICATION OF CONJUGATED DIOLEFINS

Diolefin	Derivatives prepared	M. P. of derivative, ° C.
1,3-Butadiene	1,2,3,4-Tetrabromobutane	
	High-melting form	116
	Low-melting form	38.5-39
	1,4-Dibromo-2-butene	52
Isoprene	<i>cis</i> - 5 - Methyl - $\Delta^4$ - tetrahydrophthalic anhydride <sup>a</sup>	62.5-63.5 <sup>b</sup>
Piperylene	<i>cis</i> - 6 - Methyl - $\Delta^4$ - tetrahydrophthalic anhydride	60-61
Piperylene	1,2,3,4-Tetrabromopentane	112-113
Cyclopentadiene	Maleic anhydride addition product (probably <i>cis</i> -endomethylene-3,6-tetrahydrophthalic anhydride)	162

<sup>a</sup> Neutralization equivalent (by hydrolysis with excess alkali and back titration): calcd. for *cis*-5-methyl- $\Delta^4$ -tetrahydrophthalic anhydride, 83; found, 81.

<sup>b</sup> Mixed melting point with an authentic sample showed no depression.

butenes to demonstrate the effect of temperature, pressure, and contact time on the yield of butadiene. The yields (once-through) plotted as a function of

TABLE II  
FORMATION OF CONJUGATED DIOLEFINS BY DEHYDROGENATION<sup>a</sup>

Compounds dehydrogenated	Temp. ° C.	Contact time Sec.	Diolefin		Un-reacted charge Wt. %	Carbon Wt. % of charge
			Name	Yield Wt. % of charge		
<i>n</i> -Butenes <sup>b</sup>	600	0.75	1,3-Butadiene	18	50	11.2
<i>n</i> -Butenes <sup>b</sup>	600	0.34	1,3-Butadiene	20.6	59	4.8
3-Methyl-1-butene	600	0.5	Isoprene	21.4	34 <sup>c</sup>	12.8
2-Methyl-1-butene						
+ 2-methyl-2-butene <sup>d</sup>	600	0.39	Isoprene	22.3	44	6.2
2-Pentene	600	0.40	Piperylene	30.3	44	7.6
Cyclopentane	500	1.85	Cyclopentadiene	8.9 <sup>e</sup>	62	8.8

<sup>a</sup> Catalyst, 4 per cent chromium oxide on alumina; pressure, 0.25 atmosphere (190 mm.).

<sup>b</sup> Mixture prepared by dehydration of *n*- and *sec*-butyl alcohols over alumina at 400° C. Analysis by Podbielniak fractionation method indicated: 1-butene 51.6 per cent, 2-butene 48.3, propane 1.7, residue above butenes 3.4; total olefins by bromine water absorption 94.5 per cent.

<sup>c</sup> Most of the C<sub>5</sub> olefins recovered were the higher boiling branched-chain isomers of 3-methyl-1-butene. These are included in the 34 per cent.

<sup>d</sup> From dehydration of *tert*-amyl alcohol over alumina at 400° C. with 3-methyl-1-butene removed. This mixture boiled at 27.2-37.6° (733 mm.),  $n_D^{20}$  1.3915.

<sup>e</sup> The formation of a small amount (2.7 per cent) of cyclopentene is indicated by indirect methods.

contact time are shown in Figure 2. Contact times were calculated from the equation:

$$C. T. = \frac{pvt}{743(273 + T)[g/M + \Sigma(g'/M')]}$$

where C. T.=contact time

$p$ =mean pressure (mm. Hg)

$v$ =volume of catalyst zone, cc.

$t$ =duration of run, minutes

$T$ =av. catalyst temperature, ° C.

$g$ =grams of charge

$M$ =molecular weight of charge

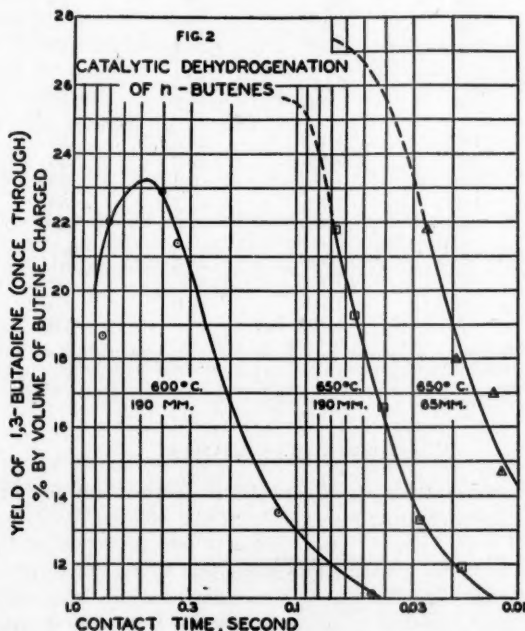
$g'$ =grams of each recovered product

$M'$ =molecular weight of each recovered product

The free space of the catalyst zone (70 per cent) is taken into account in the constant of the denominator.

These data are also given in Table III, which includes calculated recycle yields (based on analytical data). The dehydrogenation is accelerated at the same contact time by either an increase in temperature or a decrease in pressure. The best ultimate yields are obtained by recycling at low contact times, whereby the extent of side reactions is small.

Carbon formation in the dehydrogenation of olefins is considerably higher than in the dehydrogenation of paraffins, and represents over 10 per cent of the charge in some cases (Table II). This is favored by keeping the reaction products too long in contact with the catalyst and, conversely, can be



minimized by operating at short contact times (Table III). The carbon-forming characteristics of the diolefins are illustrated by an experiment in which butadiene itself was passed over the catalyst: 1,3-Butadiene was subjected to the dehydrogenation catalyst at 600° C., 0.24 atmosphere, and a contact time of 0.34 second. The products recovered included carbon 16 per cent, liquid products 6, butane 1, butenes 20, and unreacted 1,3-butadiene 40. The liquid, a result of polymerization and condensation reactions, probably contributes to carbon formation. It boiled over a wide range and contained, among other products: benzene, about 0.5 weight per cent of the 1,3-butadiene charged; styrene, about 1.0 weight per cent; and a high-boiling hydrocarbon (above 190°) with an intense blue color similar to that of azulene. (This blue color was also observed in the high-boiling liquid fraction from the dehydrogenation of 2-pentene.) Similar results were obtained with 1,3-butadiene at 450° C., 0.25 atmosphere and 3.6 seconds contact time. The products included carbon 12.1

per cent, liquid 5, butenes 34, butane 2, and 1,3-butadiene 38. The butenes and butane arise from hydrogenation of the charge with hydrogen formed by decomposition of a portion of the charge.

TABLE III  
DEHYDROGENATION OF *n*-BUTENES <sup>a</sup>

Temp. ° C.	Pressure Mm.	Contact time Sec.	Yield of 1,3-butadiene		Carbon Wt. % of charge
			Single-pass	Recycle	
			Vol. %		
600	190	0.75	18.7	37	11.2
600	190	0.7	22	42	—
600	190	0.4	22.9	—	5.1
600	168	0.34	21.4	52	4.8
600 <sup>b</sup>	197	0.12	13.5	54	1.5
600	198	0.045	11.2	62	0.8
650	192	0.068	21.8	53	2.3
650	192	0.055	19.3	56	2.1
650	189	0.041	16.6	60	1.4
650	180	0.028	13.3	69	0.9
650	168	0.018	11.9	79	0.5
650	63	0.026	21.8	51	0.9
650	63	0.019	18	60	0.8
650	63	0.013	17.0	65	0.5
650	80	0.012	14.7	69	0.4

<sup>a</sup> For source and composition of butene used in the first four experiments, see Table II, note <sup>b</sup>. The butenes used in the subsequent experiments were prepared from pure *sec*-butyl alcohol and analyzed 99.0 per cent *n*-butenes.

<sup>b</sup> Average of three experiments.

#### ACKNOWLEDGMENT

The authors express their thanks to E. E. Zetterholm for his assistance in part of the experimental work.

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# SECOND REPORT OF THE INVESTIGATION OF THE CRYSTALLIZATION OF CRUDE RUBBER \*

CHULLCHAI PARK

## INTRODUCTION

Very recently<sup>1</sup> the writer observed a small residual elongation in a stretched ribbon of smoked sheet rubber brought about by freezing, and it was found that the maximum residual elongation occurred after stretching about 200-300 per cent of the original length, and also that there was almost no elongation after stretching higher than about 700 per cent. To explain the behavior of crude rubber by crystallization, including these facts, it was assumed that the long chain molecules of rubber are in the form of large irregular spirals.

## ELONGATIONS WHEN STRETCHED RIBBONS OF RUBBER ARE FROZEN

In the present experiments, the writer first measured the small elongations of ribbons of smoked sheet rubber, stretched to different degrees, caused by freezing at about  $-40^{\circ}\text{C}$ . The results are shown in Table I. In this table the stretching

TABLE I

Stretching (in %)....	Not stretched	...	200	300	400	500	600	700	800
Elongation by freezing (in %) .....	Difficult to detect.	2	3.5	4	3	2	1	difficult to detect	

is represented as percentage of the ratio of the stretched length to the initial unstretched length, and the elongations by freezing of the specimen are expressed as percentages of the stretched lengths.

With a freezing temperature of about  $-5^{\circ}\text{C}$ , at which the previous experiment was performed, the maximum elongation occurred after stretching about 200-300 per cent of the original length, and there was almost no elongation after stretching above an elongation of about 700 per cent. However, with a much lower freezing temperature, *viz.*, about  $-40^{\circ}\text{C}$ , the position of the maximum elongation by freezing changed to an elongation of about 400 per cent, and a little elongation (about 1 per cent) was still detected at the high elongation of about 700 per cent, as shown in Table I.

## CHANGE OF THE X-RAY DIFFRACTION PATTERN, BY FREEZING, OF A STRETCHED RIBBON

It was reported in the previous paper that when a ribbon of rubber kept slightly stretched in an uncrystallized state is frozen, it gives an imperfect fibre diagram by taking the direction of stretching as its fibre axis. This point was re-examined more minutely in the present experiments, by using the same freezing camera as was used before, which was especially suited to keep the specimen frozen during the whole exposure of the photographic plate to the dif-

\* Reprinted from the *Memoirs of the College of Science, Kyoto Imperial University, Japan*, Series A, vol. 22, No. 4, pages 259-267, July 1939.

fracted x-rays. With a ribbon of smoked sheet rubber, which was stretched 200 per cent, it gave only a diffuse amorphous halo at room temperature, as shown by Fig. 1A in Plate I, but when frozen in the stretched state at about

## PLATE I

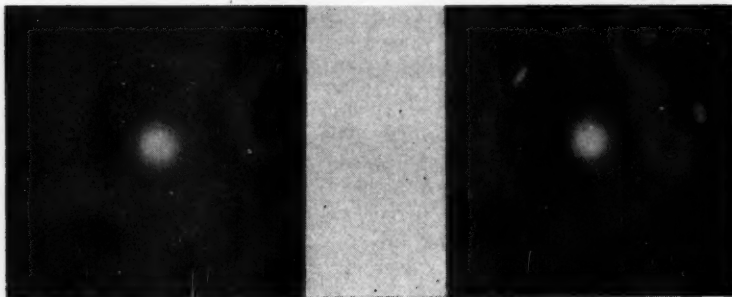


FIG. 1A.

FIG. 1B.

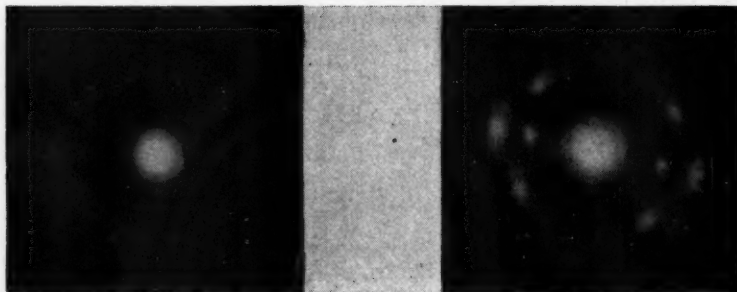


FIG. 2A.

FIG. 2B.

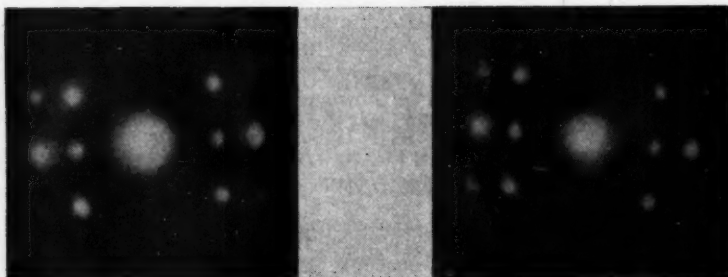


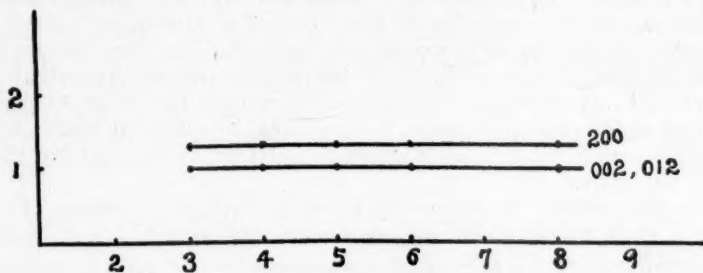
FIG. 3A.

FIG. 3B.

$-20^{\circ}\text{C}$ , it gave a fibre diagram of medium intensity superimposed on the background of the diffuse halo much diminished in its intensity, as shown by Fig. 1B of Plate I. With a ribbon stretched 300 per cent, a very faint fibre dia-



gram at room temperature became sharp and very intense by being frozen at about  $-20^{\circ}\text{C}$  with the same exposure, as is seen by comparing the two diffraction photographs reproduced in Figures 2A and 2B of Plate I. The diffuse amorphous halo almost disappeared in this case. With a high degree of stretching such as 800 per cent, the crystallization of the rubber molecules in the fibrous manner is almost completed even at room temperature, and any further accomplishment of crystallization by freezing could scarcely be detected as shown in Figures 3A and 3B of Plate I. These facts seem to show that the fairly well straightened but still not crystallized chain molecules of rubber, which exist in large numbers in low stretched ribbon, fit together to form a crystal lattice of aligning fibre form by freezing, and that this is the cause of the occurrence of a



Stretching degree in fold at room temperature.

FIG. 1A.

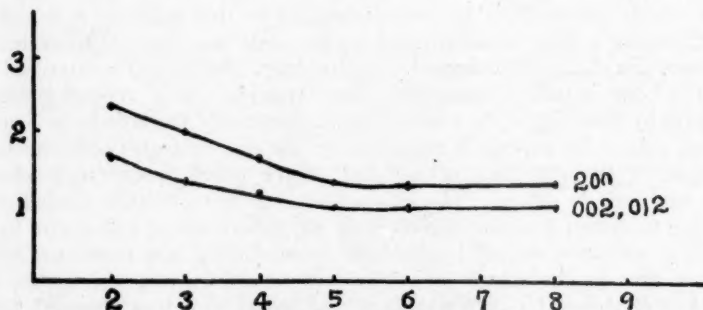
Stretching degree in fold at  $-20^{\circ}\text{C}$ .

FIG. 1B.

small elongation in the stretched direction by freezing and, moreover, that the majority of the rubber molecules are already arranged at room temperature in a crystal lattice in a fibrous state with high degree of stretching, resulting in no more crystallization and no more elongation in the stretched direction by freezing.

The lengths of the short arcs of the diffraction spots due to an imperfect fibrous arrangement of the rubber molecules, which was caused by stretching, were measured roughly and plotted in Figure 1 in reference to the stretched degree. In doing so, the most intense spots  $A_1$  (200),  $A_2$  (002) and  $I_2$  (012)<sup>2</sup> were chosen. In taking the diffraction photographs, the distance between the sample and the plate was 3.65 cm. and the diameter of the circular slit was 0.12 cm., and these were kept the same throughout the present experiment. As

the length of each arc of the diffraction spots remained the same at room temperature for various degrees of stretching, the arc length of the spot  $A_2$  (002) obtained at room temperature was taken as unity, and the arc lengths of the other spots obtained in different conditions were measured by this standard. Fig. 1A is the result obtained at room temperature. Each length of the short arcs of  $A_1$ ,  $A_2$  and  $I_2$  remained approximately the same irrespective of the degree of stretching; but in Figure 1B, which was obtained by freezing the specimen at  $-20^\circ\text{C}$ , the arc lengths of the spots increase gradually from the normal values with decrease of the stretching below about 500 per cent. This seems to be due to the fact that, at low stretching, somewhat straightened but not crystallized chain molecules of rubber whose alignment in the stretching direction is poor, unite together by freezing to form crystallites. Consequently the alignment of the crystallites in the direction of stretching becomes worse with decrease in the degree of stretching. Contrary to this case the arc lengths of the diffraction spots obtained at room temperature remained roughly the same, irrespective of the stretching degree, as stated before. This seems to show that unification of the crystal lattice of the molecules of stretched rubber at room temperature occurs only among those whose alignment in the stretched direction is practically perfect.

All the experimental results described seem to support the theory of crystallization of crude rubber which was proposed by the writer<sup>1</sup>.

#### CHANGE OF DENSITY BY FREEZING

Next the writer measured the change by freezing in the density of ribbons of smoked sheet stretched to various degrees. For this purpose a special pycnometer having a long neck provided with a scale was used. This scale served to measure the change in volume by cooling ethyl alcohol and a stretched specimen of rubber in the pycnometer. The stretching of a rubber ribbon was performed by fastening it to a metal wire. Essentially the change in density of stretched rubber by cooling is measured by the difference between the thermal expansions of the stretched rubber and of the ethyl alcohol into which the rubber specimen is dipped. The expansion coefficient of ethyl alcohol (99.5% pure) was measured with the pycnometer; the volume of the metal wire to which the rubber specimen was to be fastened by stretching was calculated from its mass and density, the volume at a standard temperature of the rubber ribbon which was stretched by fastening it to the metal wire was obtained from its mass and the weight measured by dipping it together with the stretching wire into ethyl alcohol at the standard temperature. The change of volume of ethyl alcohol containing the stretching wire alone was measured by changing the temperature from the standard one by a definite degree, and then the change of volume of ethyl alcohol containing the stretched ribbons of rubber together with the stretched wire was measured by changing the temperature from the standard value by the same degree as above. From such measurements the volume of the stretched specimen of rubber at a certain temperature was calculated, and consequently the value of its density at that temperature was obtained from its mass.

With the procedure described above, the writer measured the density of smoked sheet rubber in the unstretched and stretched state at temperatures between  $+10^\circ\text{C}$  and  $-6^\circ\text{C}$ . The results are shown in Figure 2. As will be seen from the curves in Figure 2, the density of rubber increases with decrease in the temperature; and this tendency is especially pronounced between  $0^\circ\text{C}$

and  $-6^{\circ}\text{C}$ , where the crystallization by freezing is remarkable. As to the relation between the density and the degree of stretching, the former increases with increase in the latter at a comparatively high temperature; but at low temperatures of  $-5^{\circ}\text{C}$  or  $-6^{\circ}\text{C}$ , where crystallization easily occurs merely by freezing without stretching, the density remains almost the same for different degrees of stretching. These facts seem to indicate that a remarkable change of density of rubber, which is observed in the present experiment, is mainly due to the crystallization of rubber molecules by stretching and by freezing.

It has already been stated that when a stretched ribbon of rubber is frozen, a small elongation happens in the direction of stretching; and this elongation was attributed to straightening and alignment of the chain molecules of rubber to form a crystal lattice, chiefly in the direction of stretching. Since the density of rubber increases in this case, as stated above, a considerable amount of lateral contraction must be considered to happen simultaneously with a small elongation in the direction of stretching, by freezing. This is in fair agreement with the view that the small elongation in the stretched direction, caused by freezing, is due to straightening and alignment of the chain molecules of rubber to form a crystal lattice, chiefly in the stretched direction.

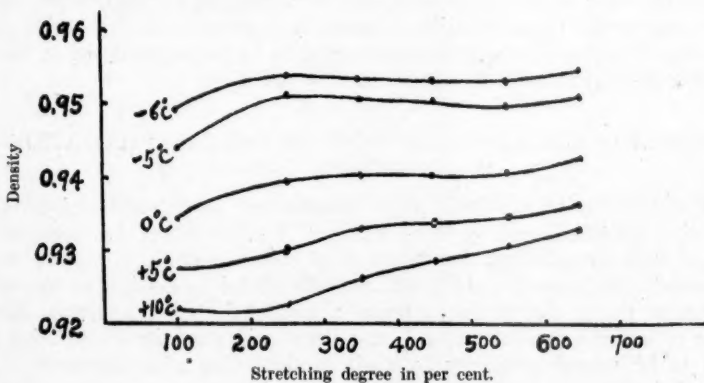


FIG. 2.

#### SUPERCOOLING OF RUBBER

When a piece of crude rubber is kept at a temperature lower than about  $5^{\circ}\text{C}$  for some time, it becomes gradually hard and loses its transparency and elasticity, and its density increases. Such rubber is usually called "frozen".

The writer immersed pieces of smoked sheet rubber suddenly into liquid air and also into a cooling mixture of dry ice and acetone whose temperature was about  $-70^{\circ}\text{C}$ . Unexpectedly the rubber became momentarily very hard like metal, but it retained perfectly the transparency which is peculiar to its amorphous state. This state continued long with continued cooling, and no change was detected even after two days. Next such a hardened piece of rubber was examined by x-rays by keeping it cooled continuously below about  $-40^{\circ}\text{C}$  after the sudden cooling to about  $-70^{\circ}\text{C}$ . It was found that the rubber was still amorphous and not crystallized in this hardened state. This is entirely analogous to the supercooled state of a liquid, and this supercooled state of crude rubber always appeared when a narrow ribbon was dipped suddenly into a cooling mixture of a temperature below about  $-35^{\circ}\text{C}$ . When the tem-

perature of the cooling mixture was higher than about  $-35^{\circ}\text{C}$ , the supercooled state was difficult to obtain and an ordinary frozen, *i. e.*, crystallized, state usually developed. As was considered before, the fitting of the chain molecules of rubber into the lattice of the rubber crystal is caused primarily by their straightening and alignment in the same parallel direction. Thus when a piece of crude rubber is suddenly cooled to such a low temperature as below  $-35^{\circ}\text{C}$ , micro-Brownian movements of every part of the long chain molecules of rubber are so much weakened suddenly that the straightening and the alignment necessary for crystallization can no more take place; consequently the chain molecules of rubber cohere tightly by sudden and severe cooling in an amorphous way just as they were at room temperature before cooling.

As to the density of the supercooled specimen of smoked sheet rubber, the writer measured it roughly by immersing a supercooled specimen into ethyl alcohol contained in a long necked pycnometer cooled to about  $-70^{\circ}\text{C}$ , and by measuring the volume of the supercooled specimen from the increase of volume of the ethyl alcohol. The value of the density thus measured was about 0.91-0.92 at about  $-70^{\circ}\text{C}$ , and was found to be of the same order as that at room temperature. This fact indicates that a remarkable increase in the density of crude rubber by freezing and stretching, as was mentioned before, is mainly due to the transformation from an amorphous to a crystalline state. Supercooling of rubber as observed above seems to be very interesting in various ways, and a more detailed investigation is now going on.

#### A DIAGRAMMATIC REPRESENTATION OF THE CRYSTALLIZATION OF RUBBER

The crystallization of rubber is very complicated; it crystallizes by cooling and by being stretched, and by being strained in other ways. An exact understanding of such complicated phenomena is of course very far from our reach; but a general idea, even if only rough, is very useful in getting at the truth. In the former paper the writer proposed a model of rubber molecules having the shape of a large, irregular spiral, and their unification in crystallizing was supposed to be caused primarily by their straightening and alignment in the same parallel direction. Thus crystallization and melting were explained by comparing the attractive force between the neighboring chain molecules side by side and the contractive force along the axis of the large irregular spiral of the rubber molecule. In Figure 3, the manner in which these forces change with temperature is shown qualitatively by the curves drawn in full and broken lines, respectively. At a temperature higher than the freezing one, the attractive force between the neighboring chain molecules side by side is lower than the contractive force along the spiral axis; however, when the temperature is lowered below the freezing temperature, the former force becomes much stronger than the latter, and crystallization by freezing takes place in this temperature range. Thus the transition from the amorphous to the crystalline state and *vice versa* occurs at point F, where the two curves ABFCD and EFGH cross each other. When a rubber ribbon is stretched sufficiently, *i. e.*, to about 8 times its original length at a temperature above freezing temperature, the contractive force along the spiral axis is compensated by the force applied externally by stretching, leaving only the attractive force between the neighboring chains side by side to act to crystallize in a fibrous manner. The crystallizing force in this state is shown by the dotted line BJ in Figure 3 as the continuation of the frozen state AB. Next when a thin ribbon of rubber is cooled suddenly



to such a low temperature, *e. g.*, below about  $-35^{\circ}\text{C}$ , the spiral rubber molecules have no time to be straightened and to fit into the crystal lattice themselves, so that crystallization is surpassed by the amorphous state down to the lowest temperature to which it is cooled, and remains so for a long time in consequence of the want of thermal agitation necessary for it to crystallize. The contractive force along the spiral axis in such a supercooled state is represented by curve GI, which is drawn by a dotted line as the continuation of curve HG. The attractive force between the neighboring chains side by side is of course in this case much smaller than the contractive force along the spiral axis.

Let us suppose roughly that the potential energy of a rubber molecule is of two kinds: (1) that of the contractive force along the spiral axis of the rubber molecule, and (2) that of the attractive force between the neighboring chains of rubber molecules side by side. In Figure 4 such potential energy per molecule of rubber is considered in relation to the change of temperature, and this is represented qualitatively by a curve drawn in full line. In this curve the part

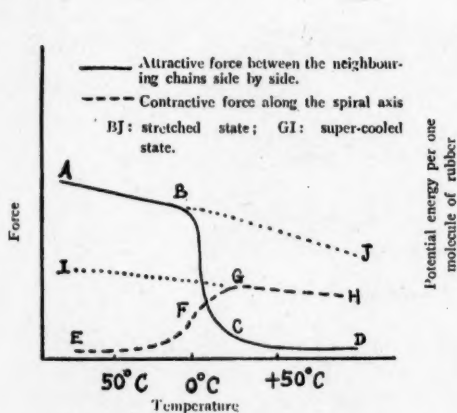


FIG. 3.

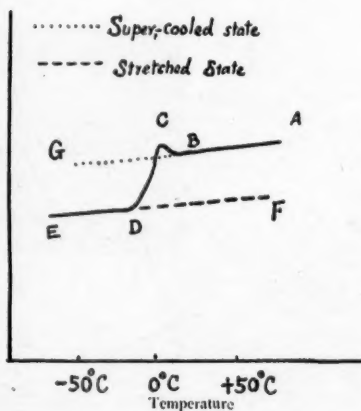


FIG. 4.

AB corresponds to the amorphous state above the freezing temperature, and the part DE corresponds to the crystallized state below the freezing temperature; and the transition from the amorphous state to the crystallized state is considered to occur along the part BCD. The presence of a small maximum at the point C is due to the increase of the potential energy by the rubber molecules being straightened before crystallization. As is well known the transformation of rubber from the amorphous to the crystalline state and *vice versa* by change of temperature is accompanied by a considerable time-lag and hysteresis; and the phenomenon of supercooling, as was stated before, is nothing but an extreme case of such a time-lag and hysteresis. The occurrence of such remarkable time-lag and hysteresis effects in the process of transformation seems to be well understood by the presence of a small maximum at C in the potential curve drawn in Figure 4, because to overcome that maximum, that is, for the chain molecules to be straightened, a considerable amount of kinetic energy due to the micro-Brownian movement in the molecules is necessary. Lastly as to the crystallization by sufficient stretching at a temperature above the crystallization temperature, it seems natural to consider that the



potential energy increases gradually with temperatures as the continuation of part ED of the potential curve, as is represented by curve DF in the figure, because any remarkable indication of the change of phase in the stretched *i. e.*, crystallized state, is not detected on passing the crystallization temperature.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to Assistant Professor K. Tanaka and S. Shimadzu for the facilities afforded to him during the present experiments.

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# THE LATTICE OF RUBBER \*

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The lattice of rubber has already been the subject of a number of investigations<sup>1</sup>. All the unit cells suggested in these papers give an x-ray density which is far higher than the measured one (8-10 per cent). Furthermore, in all Weissenberg pictures published, it is striking that the equator reflection  $A_2$  is much longer than  $A_1$  and  $A_3$ . We believe therefore that  $A_2$  is not a single

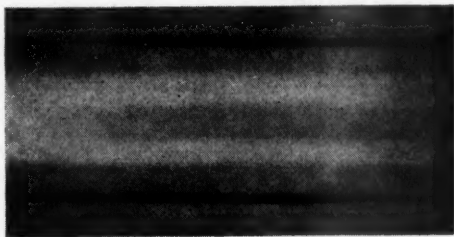


FIG. 1.—Weissenberg picture of  $A_2$ .

reflection and that the angle between  $A_1$  and  $A_2$  is not  $90^\circ$  or nearly  $90^\circ$ . While we investigated this question experimentally, Morss<sup>2</sup> published a paper, also assuming that  $A_2$  is a double reflection and making the assumption of double orientation. He calculated the unit cell for a number of angles and found an agreement with the observations at the angle of  $70.5^\circ$ . The cell contains 8 chains.

By simultaneously stretching and squeezing a piece of latex film we got a sample with rather good higher orientation. A Weissenberg picture shows the splitting of  $A_2$  into two reflections of equal intensity and shape (see Figure 1). The angle between the two maxima is  $39.2^\circ$ . The splitting is shown by all reflections except those of two zones perpendicular to each other, one of them containing  $A_1$  and  $A_3$ . Therefore there are two directions perpendicular to each other which are crystallographic directions. Because, as is known, the best orientated rubber samples give sharp diatropes, there is a third crystallographic direction perpendicular to the two others. For that reason the rubber lattice can be described as pseudorhombic. The smallest cell consistent with the diffraction data is:  $a=8.97\text{\AA}$ ,  $b=8.20\text{\AA}$  and  $c=25.2\text{\AA}$ . The same cell described in monoclinic parameters:  $a=8.97\text{\AA}$ ,  $b=8.20\text{\AA}$ ,  $c=26.7\text{\AA}$  and  $\beta=70.4^\circ$ , which is about the same cell as given by Morss. A smaller monoclinic cell would not be consistent with the reflections observed. The cell contains 16 isoprene units (8 chains). The calculated density is 0.97, in agreement with 0.965, the highest measured value for stretched rubber.

\* Reprinted from *The Journal of Chemical Physics*, Vol. 8, No. 1, page 127, January 1940.

The determination of this unit cell is unequivocal, but it is not completely satisfactory. The cell seems too large and the number of missing spectra is about 90 per cent; the equator alone could be explained by a cell of  $\frac{1}{2}$  of the large cell, containing only one chain. But a smaller unit cell can exist only if there are several structures present simultaneously (dimorphism). One of the cells has to be monoclinic because of the diatropes, the other may be triclinic, because the double orientation would give in any case the monoclinic symmetry observed in the Weissenberg patterns of the layer lines. All reflections would be explained by two unit cells:  $M_2$ , monoclinic,  $a=8.97\text{\AA}$ ,  $b=8.20\text{\AA}$ ,  $c=6.68\text{\AA}$ ,  $\beta=70.4^\circ$ , containing 2 chains and  $T_1$ , triclinic,  $a=6.12\text{\AA}$ ,  $b=8.20\text{\AA}$ ,  $c=6.99\text{\AA}$ ,  $\alpha=73.2^\circ$ ,  $\beta=64.1^\circ$ ,  $\gamma=47.3^\circ$ , containing 1 chain. Whether or not this assumption is justified has to be determined by further experiments.

This investigation was carried out in 1938 in Geneva. The authors wish to thank K. H. Meyer for his constant interest in the progress of this work. The details of the investigation will be published elsewhere.

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<sup>2</sup> Morse, *J. Am. Chem. Soc.* **60**, 232 (1938).

# ULTRAVIOLET IRRADIATION OF RUBBER \*

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## INTRODUCTION

It is a well known fact that exposure to light produces marked changes in the properties of rubber, whether in the free or the dissolved state. Attempts at various times have been made to study some particular property before and after exposure to ultraviolet or visible light. Thus the effects of light on the viscosity<sup>1</sup>, surface tension<sup>2</sup>, aging<sup>3</sup> and vulcanization<sup>4</sup> of rubber have been studied, but the conclusions of different workers are not always in agreement, a circumstance which can be understood if one remembers that the experimental conditions are very difficult of control and even a small variation of conditions is likely to lead to large variations in the results. Special care was therefore taken in the present case to control the conditions of experimentation, and the present paper deals with the effect of ultraviolet irradiation on the light absorption of rubber in different solvents.

Lewis and Porritt<sup>5</sup> and Scheibe and Pummerer<sup>6</sup> have measured the ultraviolet absorption of rubber dissolved in ether and hexahydrotoluene, and have found that the absorption is of a general character, reaching an appreciable magnitude below 2700 Å.U. and tending to a maximum at about 2000 Å.U. Absorption of light by a material medium is closely related to the state of the molecules and atoms of the medium and is, as a general rule, unaffected by the nature of the solvent, except insofar, of course, that the absorption of the solvent will be superimposed on that of the solute. At the same time it is obvious that if the solvent exerts any action on the solute molecule so as to change it materially, absorption might be expected to change with the solvent. It was therefore considered possible that some information on the state of the rubber in different solvents could be obtained by studying its light absorption when dissolved in different solvents. The choice of solvents was however limited by the fact that a high ultraviolet transparency was essential for the experiment, while at the same time there should be a reasonable expectation that the solvents would cause different effects on rubber. It is known from the work of Pummerer<sup>7</sup> that the molecular weight of rubber changes from a very large value in benzene solution to a very much lower value in menthol solution, and it was therefore decided to use two non-polar solvents and two polar solvents for the study.

## EXPERIMENTAL

The same kind of rubber was used in all the experiments, and it was prepared by repeated purification of pale crepe rubber. The chief impurity in pale crepe rubber is about four to five per cent of nitrogenous substances present as proteins and resins, and to purify the rubber, it was cut into small bits, washed in flowing water for one or two days and finally rinsed in three or four changes of distilled water. It was then dried over calcium chloride in a

\* Reprinted from the *Proceedings of the Indian Academy of Sciences*, Vol. 10, No. 3, pages 186-196, September 1939.

desiccator filled with carbon dioxide. The dry rubber was dissolved in benzene and about 200 cc. of this solution were taken in a liter bottle, mixed with an equal amount of a 2 per cent solution of caustic alkali and the whole was shaken well in a machine for an hour. A small amount, about 20 cc. of acetone, was then added to the mixture and the shaking was continued for another hour. Excess of acetone was then added, and this completely precipitated the rubber in a fine form which, however, on standing for some time united as a compact mass of great tenacity. The clear liquid was then decanted off and the precipitated rubber was dissolved in a fresh quantity of benzene and the previous treatment was repeated. A Kjeldahl estimation of the precipitated rubber showed a rapidly decreasing percentage of nitrogen content after every successive operation, until after about six repetitions the nitrogen content was quite negligible. The finally precipitated rubber was washed for a long time in flowing water to remove the alkali completely until phenolphthalein indicated the absence of alkali in the washing. It was then rinsed in distilled water and dried over calcium chloride in a vacuum desiccator until two weighings, with an interval of twenty-four hours, showed no appreciable difference.

Small weighed pieces of this rubber were cut into minute bits and placed in a stoppered graduated cylinder, from which air had been previously displaced by a slow prolonged current of argon. The pure solvent, freed from dissolved air by prolonged boiling under reduced pressure with a reflux condenser, was added to make up a definite volume of solution. It was usually found that in about forty-eight hours a clear homogeneous solution was obtained. In the case of menthol, a definite amount of menthol was taken in a Kjeldahl flask, from which the air had been displaced with argon, and kept in a molten state by immersing the bulb in a beaker of warm water. A weighed quantity of rubber in small bits was added to the solvent and the temperature was maintained at about 45° C until all the rubber was thoroughly dissolved. During the experiment of measuring the absorption, a gentle current of warm air was kept blowing on the cell to keep the solution in the liquid state.

For the measurement of absorption, a Hilger Spekker Photometer was used in conjunction with a Hilger quartz spectrograph (E 316), and golden iso-zenith plates were employed for taking the photographs. No special sensitizing of the plates was found necessary, since the limit of ultraviolet transparency of the solutions was reached earlier than the limit of the sensitivity of the plates. The source of illumination was a condensed spark discharge between tungsten-steel electrodes from a high tension induction coil fed with 220 V 25 ~ A.C. on the primary side, the current input being about 3 amperes. To obtain comparable results the solutions were all of the same concentration of five grams of rubber in a liter of solution, and the length of the absorbing column was in all cases 5 mm. During an experiment, the solution contained in a cell of 5 mm. length with optically ground quartz end-plates was placed in the path of one of the beams, while a similar cell containing the pure solvent was placed in the path of the other beam, thereby automatically compensating the absorption due to the solvent. When the measurement was completed, the two cells in their own special clamps were supported in front of a quartz mercury lamp at a distance of 20 cm., the incident light being as nearly normal to the end-plates as possible. Care was taken to avoid even tiny air bubbles inside the cells, and a fan was kept blowing on the cells from the direction of the cells to the arc so that hot air in the vicinity of the arc was blown away from the solution. A sensitive thermometer suspended by the side of the solutions did not indicate any noticeable change of temperature in three hours.



## RESULTS

From the photographs obtained, the points of equal intensity of the two spectra for various values of the extinction coefficient were read off in wavelength units. The results are given in the following tables. The absorption curves obtained by plotting the various values obtained are given in the figures, the extinction coefficients along the x-axis and the corresponding equality wave lengths along the y-axis. The full length curves in the figures represent the absorption before exposure, and the dotted curves and the chain-dotted curves represent the same after 3 hours' and 6 hours' exposure, respectively.

## DISCUSSION

The results in general confirm the earlier observations that the light absorption of rubber is very small in the visible region, appreciable below 2700 Å.U. and tends towards a maximum at about 2000 Å.U., and that throughout it is of a general nature and not selective. The remarkable observation, however, of the present investigation is the fact that the behavior of rubber in menthol and ethylene chloride is different from that in heptane and in cyclohexane. In the polar solvents, menthol and ethylene chloride, ultraviolet radiation increases the light absorption of rubber, whereas in the non-polar solvents, heptane and cyclohexane, it diminishes the absorption. In other words, due to ultraviolet irradiation, rubber becomes more transparent when dissolved in non-polar solvents and less transparent when in polar solvents. Obviously any explanation of this behavior should take into account the solvent effect on rubber, particularly with respect to the size of the molecule, the formation of micelles, the degree of solvation, and so on. Here, however, one has to tread rather very doubtful ground, since there is a great deal of disagreement even among chemists on the molecular state of rubber in different solvents. It is known from the work of Staudinger<sup>8</sup> and others that rubber exists as enormous macromolecules in non-polar solvents like benzene, while it would appear from the work of Pummerer<sup>7</sup> that, in polar solvents like menthol, the molecule is very much smaller. The fact that on removal of the solvent, rubber from menthol solution behaves in an identical manner with rubber from benzene solution leads to the conclusion that the essential chemical nature is unaffected by solvents but that the size of the molecule in the solvent is affected. Examination of rubber by means of x-ray and electron-diffraction methods leads one to the conclusion that a micelle structure is not very likely, if by micelle is meant a large stable clustering of molecules<sup>9</sup>. Also from the high elasticity and high extensibility of rubber, it is known that the van der Waal forces between rubber molecules should be very small, indeed too small to warrant any stable micellar structure. Even if weak van der Waal forces are assumed to produce some kind of loose micelles, it is hard to understand how a polar solvent has a better chance of breaking down the van der Waal forces than a non-polar solvent. If, therefore, one is forced to admit that rubber in solution is truly molecular and not micellar, it is rather difficult to escape the conclusion that in polar solvents a definite breaking down of the molecule takes place. The cause of this breaking down of the molecule may be simply the field of force of the solvent molecules, and then it is quite natural that on removal of the solvent and the corresponding field of force, the original size of the rubber molecule should be restored<sup>10</sup>. Several workers in the field have pictured the rubber molecule as a spiral or a snake-like kinked chain, but whatever model be assumed, it is obvious that in a giant molecule of the kind that rubber is supposed to be,

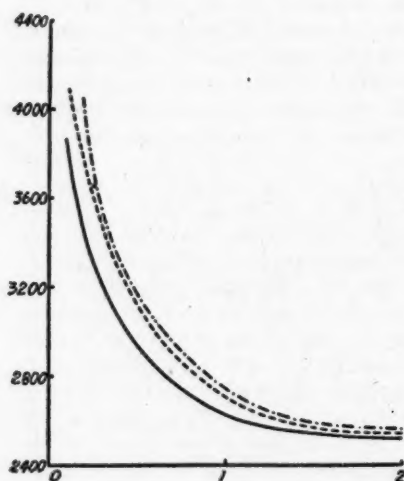


FIG. 1.—Rubber in menthol.

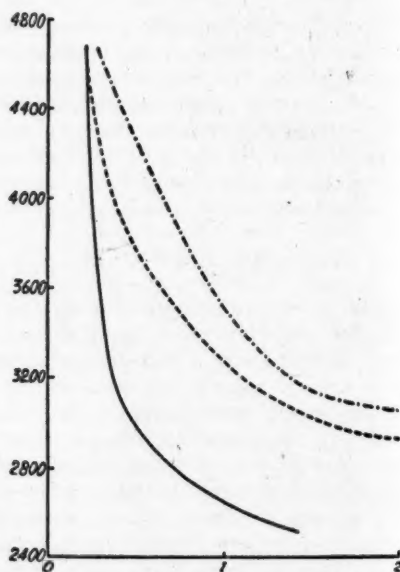


FIG. 2.—Rubber in ethylene chloride.

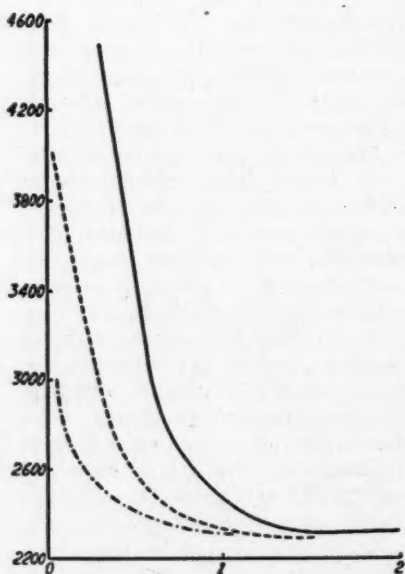


FIG. 3.—Rubber in cyclohexane.

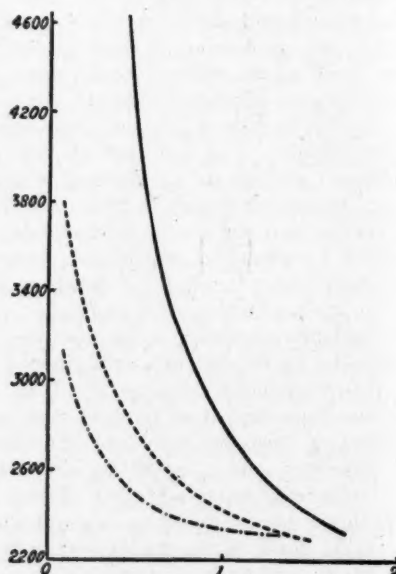


FIG. 4.—Rubber in heptane.

TABLE I  
ABSORPTION OF RUBBER DISSOLVED IN MENTHOL

No.	Extinction coefficient $\log I_0/I$	Wave length of equal intensity in Å. U.		
		Before exposure	After 3 hours' exposure	After 6 hours' exposure
1	0.1	3850	4100	—
2	0.2	3470	3850	4050
3	0.3	3210	3360	3580
4	0.4	3050	3250	3270
5	0.5	2980	3150	3170
6	0.6	2850	3050	3070
7	0.7	2780	2950	2960
8	0.8	2690	2820	2830
9	0.9	2675	2770	2780
10	1.0	2650	2730	2740
11	1.1	2625	2650	2650
12	1.2	2600	2620	2620
13	1.3	2590	2610	2610
14	1.4	2585	2585	2600
15	1.5	2575	2580	2590
16	1.6	2560	2575	2585
17	1.7	2530	2565	2575
18	1.8	2520	2560	2570
19	1.9	2515	2555	2570
20	2.0	2510	2550	2570

TABLE II  
ABSORPTION OF RUBBER IN ETHYLENE CHLORIDE

No.	Extinction coefficient $\log I_0/I$	Wave length of equal intensity in Å. U.		
		Before exposure	After 3 hours' exposure	After 6 hours' exposure
1	0.1	5000	~ 5000	> 5100
2	0.2	4500	4700	5050
3	0.3	3650	4200	4575
4	0.4	3080	3950	4400
5	0.5	2980	3740	4225
6	0.6	2850	3620	4100
7	0.7	2800	3530	4000
8	0.8	2710	3460	3850
9	0.9	2690	3370	3710
10	1.0	2630	3280	3550
11	1.1	2620	3150	3450
12	1.2	2580	3100	3210
13	1.3	2540	3090	3180
14	1.4	2520	3080	3130
15	1.5	—	—	—
16	1.6	—	3010	3115
17	1.7	—	—	—
18	1.8	—	2990	3100
19	1.9	—	—	—
20	2.0	—	2930	3050

TABLE III  
ABSORPTION OF RUBBER IN CYCLOHEXANE

No.	Extinction coefficient $\log I_0/I$	Wave length of equal intensity in Å. U.		
		Before exposure	After 3 hours' exposure	After 6 hours' exposure
1	0.1	> 5100	3770	2920
2	0.2	4950	3350	2580
3	0.3	4500	2980	2510
4	0.4	4000	2780	2480
5	0.5	3520	2570	2435
6	0.6	3080	2445	2400
7	0.7	2770	2425	2370
8	0.8	2690	2390	2350
9	0.9	2590	2355	2330
10	1.0	2440	2345	2315
11	1.1	2370	2345	2310
12	1.2	2355	2330	2305
13	1.3	2340	—	2305
14	1.4	2330	2320	2305
15	1.5	2325	—	2305
16	1.6	2325	—	—
17	1.7	2325	—	—
18	1.8	2325	—	—
19	1.9	2325	—	—
20	2.0	2325	—	—

TABLE IV  
ABSORPTION OF RUBBER IN HEPTANE

No.	Extinction coefficient $\log I_0/I$	Wave length of equal intensity in Å. U.		
		Before exposure	After 3 hours' exposure	After 6 hours' exposure
1	0.1	> 5000	3780	3110
2	0.2	> 5000	3300	2840
3	0.3	> 5000	3110	2670
4	0.4	4700	3000	2550
5	0.5	4300	2710	2500
6	0.6	3650	2560	2460
7	0.7	3350	2520	2400
8	0.8	3050	2490	2360
9	0.9	2930	2460	2350
10	1.0	2850	2400	2340
11	1.1	2710	2365	2335
12	1.2	2590	2335	2325
13	1.3	2480	2330	2315
14	1.4	2420	—	2310
15	1.5	2360	—	—
16	1.6	2340	—	2300
17	1.7	2330	—	—

there should occur periodical places in the molecule where the bonds are definitely angular instead of linear, and it is just at these angular points of weak binding<sup>11</sup> that one might expect the field of polar molecules to exert their disruptive action.

It appears, accordingly, justifiable to assume that in non-polar solvents, rubber exists in a highly polymerized condition, whereas in a polar solvent the degree of polymerization is at a much lower level. Furthermore it is known from the work of Asano<sup>12</sup> that ultraviolet light in the absence of oxygen produces both

polymerization and depolymerization of rubber. Now if two opposite changes, like polymerization and depolymerization, can be induced by the same cause in a system, evidently, by the law of mass action the course of changes will be greatly determined by the initial conditions of relative concentration of the different components. Thus if the initial condition is one of low degree of polymerization, as in polar solvents, the effect of ultraviolet light would be to induce a higher stage of polymerization and *vice versa*. We can thus picture a tentative explanation of the difference in behavior in polar and non-polar solvents. Again, an examination of the curves shows that, in the major part of the region, before exposure to ultraviolet light, the light absorption of rubber is greater in non-polar solvents than in polar solvents. This would lead to the assumption that, in the more polymerized state, rubber has got a greater absorbing power than in the less complex state. The effect of ultraviolet irradiation in the case of polar solvents which leads to the formation of more complex molecules will therefore lead to increased absorption, whereas in the case of non-polar solvents it should lead to the opposite effect.

To see if any support to the above concept can be had from other considerations, a preliminary study of the effect of ultraviolet irradiation on the viscosity and surface tension of rubber solutions was made with rubber dissolved in heptane, cyclohexane, ethylene chloride and cyclohexanone. As before, the solvents were freed of any dissolved air by boiling under reduced pressure, and the solutions were made in vessels from which the air had been previously displaced by a slow prolonged stream of argon. Viscosity was measured by means of an Ostwald viscometer, and surface tension by means of a Du Nuoy balance. The solutions in non-polar solvents had an initial viscosity more than one-hundred times that of the solvent, but this value showed a rapid decrease with increasing amount of irradiation with ultraviolet light, until at the end of about one-hundred hours of irradiation the viscosity had come down nearly to that of the solvent. In the case of the polar solvents the initial viscosity was only about four or five times that of the solvent, and irradiation for over a week only reduced it to about three-fourths of its previous value. Surface tension showed hardly any appreciable change, even after a week's exposure in the case of all solutions. It would appear from the above observations that ultraviolet light breaks down the rubber molecule in non-polar solvents, whereas in polar solvents there is apparently not much effect. This might reasonably be anticipated if we postulate the existence of fairly small molecules in polar solvents, which have been broken down to the minimum stable size by the action of the solvent. This however could not tell us anything definite as to whether actual polymerization does not take place by irradiation in polar solvents. It would be interesting to seek for independent evidence on molecular dimensions under different conditions by studying the depolarization of scattered light by the method employed by Krishnan<sup>13</sup> in his study of colloids and liquid mixtures.

In conclusion, the author wishes to record his grateful thanks to his Professor, Sir C. V. Raman, for his kind interest in the course of the work.

#### SUMMARY

The absorption of light by rubber when dissolved in polar and non-polar solvents was measured before and after exposing the solutions to ultraviolet light in the absence of air. It was found that irradiation with ultraviolet light makes rubber more transparent when in non-polar solvents and less transparent



when in polar solvents. The state of rubber in solution is reviewed in the light of present-day knowledge, and a tentative explanation of the absorption phenomenon is suggested on the assumption that the rubber molecule in a polar solvent is depolymerized by the field of the solvent molecule and that ultraviolet light produces both polymerization and depolymerization of rubber, according as rubber initially is in a low or high state of polymerization. A probable support to this concept from measurements of viscosity is indicated.

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# MECHANISM OF POLYMERIZATION REACTIONS \*

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The peculiar properties possessed by molecules consisting of long chains of atoms linked together by primary valence forces are as yet imperfectly understood. Both naturally occurring and synthetic substances of this type are now familiar in a large variety of forms, of which rubber and cellulose are well-known examples of the former type. The problem may be attacked from two points of view. On the one hand by an investigation of the properties of large molecules something may be learned about molecular structure; on the other an attempt may be made to build such molecules synthetically to a predetermined pattern so that a correlation between structure and behavior may be established. This article will be solely concerned with the second aspect of the subject. Here the general problem is to carry out the synthesis under rigidly controlled conditions in order that the precise mechanism of molecule building may be determined with absolute certainty.

In physical chemistry there exists a reasonably satisfactory kinetic theory of chemical reactivity which allows one to formulate the mechanism of a reaction from observations of the effect of various factors on the velocity of that reaction. The theory has been most highly developed for gaseous reactions, and it would therefore seem most logical for the present to confine attempts to the elucidation of the mechanism of gaseous polymerizations. This automatically excludes the polycondensation method of producing large molecules. We are left then to consider the polymerization reactions of ethylene derivatives. Observations on liquid phase polymerization are legion, starting from the earliest attempts to produce synthetic rubber to the standardized technique now employed for the manufacture of transparent resins and synthetic rubbers. Experiments on gaseous polymerization are few in number for the simple reason that it is not an easy matter to induce the reaction to go. High temperatures, though favoring reaction, invariably result in the production of polymers of low molecular weight. By starting polymerization photochemically, this difficulty may be overcome, with the additional advantage that precise control of the initiation of polymerization becomes possible. The only disadvantage here is the simple molecules ethylene, acetylene and isoprene do not polymerize readily; in fact, they tend to decompose on absorption of radiation, thus precluding any thorough investigation of their reactions. Fortunately, however, a number of slightly more complicated molecules of the general type:  $\text{CH}_2=\text{CXY}$ , where  $\text{X}=\text{COOCH}_3$ ,  $\text{COCH}_3$ ,  $\text{CN}$ ,  $\text{Cl}$  and  $\text{Y}=\text{H}$ ,  $\text{CH}_3$ , etc., polymerize readily and, indeed, are in every way suitable for the type of work under discussion. The introduction of the  $\text{X}$  group not only facilitates the polymerization reaction itself, but it also extends the absorption region of the molecule to longer wave lengths, the group thus functioning as a chromophore. It is the combination of these two effects which makes the photopolymerization a practicable proposition. It is of interest to note that one factor alone is not sufficient. For example, methyl crotonate:  $\text{CH}_3\text{CH}=\text{CH}\cdot\text{COOCH}_3$ , absorbs light to the same extent as methyl methacrylate but does not exhibit any tendency to polymerize.

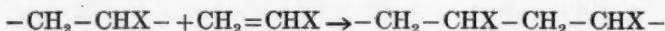
\* Reprinted from the *Transactions of the Institution of Rubber Industry*, Vol. 15, No. 4, pages 209-220, December 1939.

In fact, this appears to be a general observation for monoethenoid compounds. The  $\text{CH}_2=\text{C}<$  structure is the first essential for the occurrence of polymerization. If only one of the hydrogen atoms is replaced by a methyl group, for instance, polymerization is completely inhibited. The same behavior is exhibited by the chloroethylenes.  $\text{CH}_2=\text{C}(\text{Cl})_2$  polymerizes readily,  $\text{CHCl}=\text{CHCl}$  (*cis* or *trans*) will not polymerize at all.

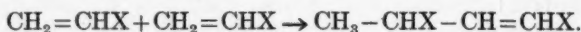
To simplify the subsequent discussion as far as possible, attention will for the most part be devoted to three molecules, namely, methyl methacrylate:  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$ , methyl acrylate:  $\text{CH}_2=\text{CH}\cdot\text{COOCH}_3$ , and chloroprene:  $\text{CH}_2=\text{C}\cdot\text{Cl}-\text{CH}=\text{CH}_2$ , the first two forming clear resins and the latter a rubber.

Absorption of light by methyl methacrylate begins to be noticeable at about 2900 Å, rises slowly to 2300 Å and thereafter rapidly. Roughly speaking, light of wave length shorter than 2300 Å decomposes the molecule into methane and probably  $\text{CH}\equiv\text{C}\cdot\text{COOCH}_3$ , whereas light of longer wave length leads predominantly to polymerization. A similar type of behavior is exhibited by chloroprene, which is even more sensitive to the influence of wave length. Here wave lengths shorter than 2520 Å cause complete decomposition, with not a trace of polymerization. Thus another guiding principle becomes apparent. The molecule of monomer will only hold a certain amount of energy without rupture. Furthermore, with at least one molecule, namely, methyl isopropenyl ketone, the critical energy is so low that absorbed radiation of any wave length leads to decomposition to the exclusion of polymerization. It is not possible to say what is the minimum energy required to start polymerization because absorption of light is so feeble at long wave lengths that polymerization cannot be detected.

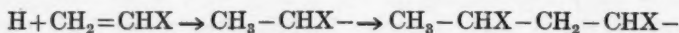
Having got polymerization started, the next problem is to find out something about the chemical nature of the process and of the subsequent growth of the polymer. Two and only two extreme possibilities may be imagined for monoethenoid compounds. The first is that a diradical is formed and then the monomeric molecules add on thus:



and so on. The second is that the double bond preserves its character but is rendered more reactive than in the normal state, with the result that the monomer adds on much more easily.



Purely energetic considerations regarding the primary process in the reaction cannot distinguish unequivocally between the two mechanisms. The difficulty can, however, be overcome in the following way. Hydrogen atoms and methyl radicals readily add on to methyl methacrylate and thereby induce polymerization to take place thus:



and so on. By carrying out the reaction in this manner, it is assured that the mechanism will involve the growth of a free radical and that the characteristics will be those of such a mechanism. These characteristics are simple and are summarized by the equation:

$$\cdot \text{Rate} = \text{const. } I^{\frac{1}{2}} (M),$$

where  $I$  is the intensity of the absorbed light and  $(M)$  the concentration of the methacrylate. Mention should perhaps be made of the method of generating

H atoms and methyl radicals. The former are produced by adding hydrogen and mercury vapor to the monomer and illuminating the system with light absorbed by the mercury vapor. The mercury atoms are thereby excited, and transfer their electronic energy to hydrogen molecules by collision, with the simultaneous production of atomic hydrogen thus:  $\text{Hg} + \text{H}_2 \rightarrow 2\text{H} + \text{Hg}$ . Methyl radicals are most conveniently made by illuminating acetone vapor, which decomposes to  $\text{CH}_3\text{CO}$  and  $\text{CH}_3$ .

Another important characteristic of free radical polymerization is that on switching off the light the reaction rate drops in a fraction of second to zero. The time required for the polymer to grow is thus small. The next problem is to determine how and why it stops growing. The fact that the rate of reaction is proportional to the square root of the intensity indicates that growth of the polymer comes to a stop when two growing polymers interact with each other. The following simple considerations will show how this is proved. If a particular live polymer be denoted by  $P_r$ , then when the reaction is going steadily its rate of production must be equal to its rate of removal, therefore:  $f(I) + k_{r-1}(P_{r-1})(M) = k_r(P_r)(M) + k_t(P)^2$ , where the first term is the rate of production of active polymers photochemically, and  $k_{r-1}(P_{r-1})(M)$  is the rate of production of the polymer from the free radical of one molecular unit smaller than  $P$ . The third term is its rate of removal to a higher polymer by interaction with the monomer and  $k_t(P)^2$  is the rate of combination of such free radical polymers. The second and third terms are very nearly of the same magnitude and therefore:

$$(P_r) = \left( \frac{f(I)}{k_t} \right)^{\frac{1}{2}}$$

But the rate of polymerization is simply:

$$\text{Rate} = k_r(P)(M) = \text{const. } (I)^{\frac{1}{2}} (M)$$

in agreement with experimental findings. In carrying out this simple calculation it has been assumed that the lifetime of the active polymer is short compared with the reaction time, and it is therefore necessary to justify this assumption by measuring the lifetime exactly.

On switching off the light, the velocity of reaction decays so quickly that it is not practicable to measure the amount of polymerization in so short a period. It is necessary then to devise some means of integrating a number of decay periods so that a sensible amount of monomer disappears. This can be done by interposing, between the reaction vessel and source of illumination, a disc out of which has been cut two 90° slots so that the vessel is only exposed for half the normal time when the disc is rotating. Suppose first the vessel is continuously exposed to radiation then:

$$\text{Rate} = \text{const. } I^{\frac{1}{2}}$$

If now the sector is rotated very slowly so that the interval between successive periods of illumination is long compared with the lifetime of the polymer, then the light is only on for half the normal period corresponding to that with complete illumination. Therefore:

$$\text{Rate}_L = \text{const. } I^{\frac{1}{2}}/2.$$

On the other hand, when the sector rotates very quickly so that the interval between successive periods of illumination is short compared with the lifetime

of the polymer, then the intensity of the light is virtually cut down by a factor of two and therefore:

$$\text{Rate}_H = \text{const.} \left( \frac{I}{2} \right)^{\frac{1}{2}}$$

The ratio of rates of high speeds to that at low speeds is therefore  $\sqrt{2}:1$ . Experimentally this is the behavior observed, the rate being independent of the rate of rotation above and below a transition region, as is shown by Figure 1. To a first approximation the exposure interval at which the change is half complete may be taken as the lifetime of the active polymer, and for the experiment shown in Figure 1, the life amounts to about  $10^{-2}$  second.

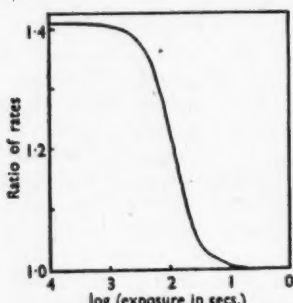


FIG. 1.—Variation of rate of polymerization with sector speed.

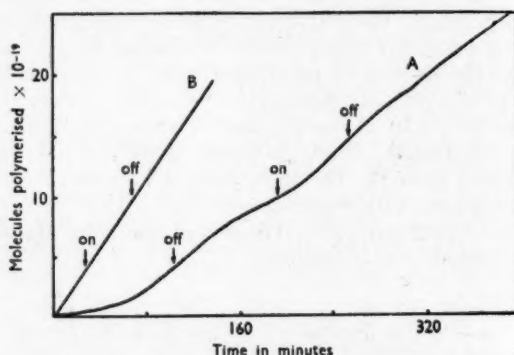


FIG. 2.—Polymerization rate as a function of time of illumination. Curve B is contiguous with A, but has been shifted to the origin to contract the time scale.

By these methods, then, the characteristics of the free radical polymerization are established. It is now necessary to consider the normal direct polymerization. Here the behavior is quite different. If the number of molecules polymerized is plotted against time, it will be observed from Figure 2 that the rate gradually increases with time on switching on the light. On switching off the light, however, the rate of polymerization decreases only slowly. On switching on again, the speed increases until after a sufficient period of illumination it does not matter whether the light is on or off, the rate of polymerization remains unaltered. This continued growth in darkness may be followed for many hours, and only decays appreciably in a matter of days under the most favorable conditions. The growth in darkness occurs at the surface of the reaction vessel, though, of course, the centres for polymerization are first formed in the gas phase. The absolute rate of polymerization is now proportional to the area of the surface illuminated, and therefore the induction period observed is due to the time required to deposit the centres necessary for polymerization. It must be concluded, therefore, that in virtue of the different characteristics of the two reactions the direct photopolymerization occurs by the double bond mechanism, so that each time a monomer adds on to the polymer a double bond is produced at the end of the active polymer.

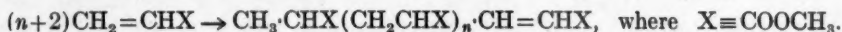
In this manner long molecules can be produced by keeping the polymer in contact with the vapor of the monomer for a sufficient time. As the activity of the polymer is apparently resident in its terminal double bond, that ac-



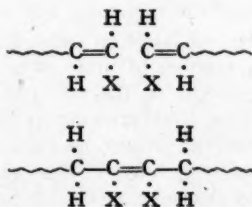
tivity may be destroyed by saturating the double bond. This may be accomplished by removing the monomer, putting in molecular hydrogen and mercury vapor, and illuminating the system with light absorbed by the mercury vapor when atomic hydrogen is produced and hydrogenates the double bond. Any other reagent likely to attack a double bond may likewise be employed to kill the active polymer.

The size of the molecules may also be decreased, for on heating the polymer to 300° C. *in vacuo*, depolymerization occurs with the production of monomer.

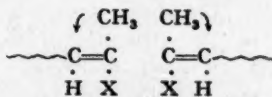
The next problem is to account for the long continued growth of the polymethacrylate. For that purpose the behavior of methyl acrylate may be considered. This molecule polymerizes rapidly when irradiated with light about 2500 Å, but is decomposed to hydrogen, and a residue if light of shorter wave length is employed. Again, therefore, there is a parallel behavior with methyl methacrylate. In contrast to the methacrylate, there is no long continued growth after the light is cut off and the active polymer dies quickly. The rate of polymerization is proportional to the square root of the light intensity, pointing therefore to the fact that growth of active molecules ceases when two such molecules collide. In view of the similarity of acrylate and methacrylate molecules, it is concluded that the growth in the acrylate reaction occurs by the double bond mechanism thus:



The termination reaction will take place in the following manner:



the essential reaction being the simultaneous migration of the hydrogen atoms to the neighboring carbon atoms. Now suppose the same type of mutual destruction were attempted by the methacrylate, then, as will be evident from the formulas given below, it would be necessary to shift simultaneously two methyl groups, which according to chemical experience is a difficult matter to



accomplish. In fact, as will be seen later, it is not easy to shift two hydrogen atoms. It would, therefore, appear that the long lifetime of such active polymers is essentially due to the fact that there is a relatively immobile group attached to the  $\alpha$ -carbon atom of the monomer. In this connection it may be recorded that chloroprene:  $\text{CH}_2=\text{C} \begin{smallmatrix} \text{Cl} \\ \diagup \\ \text{CH}=\text{CH}_2 \end{smallmatrix}$ , and methyl isopropenyl ketone:  $\text{CH}_2=\text{C} \begin{smallmatrix} \text{CO CH}_3 \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$ , can both be induced to grow in a manner similar to the methacrylate.

To get an exact quantitative measure of the tendency of a molecule to polymerize, it is essential to have precise information on the molecular statistics of growth, that is, how much energy must be acquired by the system before the monomer will add on, and how many collisions there are before this addition takes place. In the polymerization of methyl acrylate, it can be shown from the fact that the active polymers mutually destroy each other that the rate of the overall reaction is given by the composite equation:

$$\text{Rate} = \sqrt{\frac{\text{rate of starting}}{\text{rate of stopping}}} \times \text{rate of propagation.}$$

To obtain the critical energy for the addition of monomer, the temperature coefficient of the rate of propagation must be determined. But the most surprising thing about this reaction is that the overall temperature coefficient is negative, the rate decreasing rapidly with increasing temperature. The temperature coefficient of the rate of starting is practically zero, so that the temperature coefficient of the stopping reaction must be greater than that of propagation. If, however, oxygen is added to the mixture, there is a great retardation, owing to the fact that the oxygen interacts with the growing polymer and therefore prevents the occurrence of the normal mutual destruction of the active polymer. The reaction of the oxygen with the polymer is so efficient that the temperature coefficient of the stopping reaction is now zero, with the result that the temperature coefficient of the whole reaction is now positive and corresponds in fact to an energy of 4,000 calories. This, then, is the average energy which must be supplied before the monomer will add on to polymer.

Next, the absolute efficiency of addition must be determined. But it is first of all necessary to know the number of units of monomer making up the polymer, that is, the molecular weight of the polymer, and also the total number of collisions between monomer and growing polymer during its active lifetime. Estimates of the molecular weight could, of course, be made by withdrawing the polymer and utilizing one of the existing methods. However, it was desirable, if possible, to devise a method which could be used while the polymer was being grown. One obvious method would be to measure the number of molecules of monomer polymerized for each quantum of light absorbed by the system. Here, however, an assumption is made that each quantum absorbed starts off a polymerization chain. There is no justification *a priori* for making such an assumption. The difficulty can be surmounted in the following manner. An inhibitor is added to the mixture in such amount that all the polymer chains are stopped by it. Butadiene is such a substance for the acrylate polymerization and, therefore, the structure of the polymer is AAAAAAB. Fortunately, although butadiene itself undergoes polymerization, the chain length is so short that only one molecule adds on. The ratio of the number of acrylate molecules to the number of butadiene molecules which are used gives the molecular weight of the product in the inhibited reaction, from which the molecular weight in the ordinary reaction is easily obtained.

Perhaps the simplicity of the method may be emphasized by describing briefly the experimental procedure. The mixture of butadiene and acrylate is condensed by means of liquid air into a side tube attached to the reaction system and then allowed to warm. On plotting pressure against time, it will be seen from Figure 3 that first the butadiene evaporates, followed by the acrylate, so that the proportion of each may be estimated exactly. The reaction is then

allowed to go, and the distillation procedure is repeated, whereby the amounts of butadiene and acrylate used may at once be determined.

The next stage is the determination of the lifetime of the active polymer. This could, of course, be determined by the sector technique, but it may be of interest to describe an alternative method which has been used in the present instance. It again makes use of the fact that the rate of reaction is proportional to the square root of the intensity of the incident light. The lifetime of the polymer ( $t$ ) and the distance ( $x$ ) it diffuses in space are connected with the diffusion coefficient by the relationship:

$$x^2 = 2Dt.$$

If, therefore,  $x$  can be measured,  $t$  may be calculated, since  $D$  can be computed from the molecular weight of the polymer. The value of  $x$  may be determined in the following way. Two beams of light of equal intensity are projected into the reaction vessel by means of an arrangement which allows their

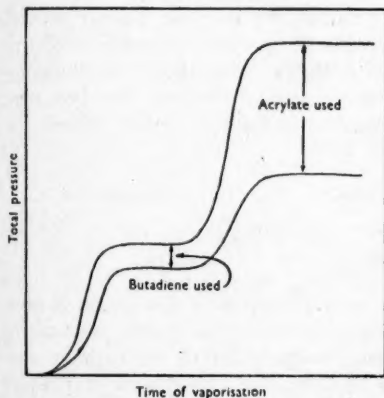


FIG. 3.—Distillation curves for butadiene-methyl acrylate mixtures before and after polymerization.

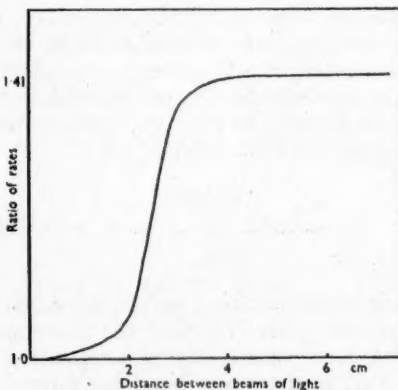
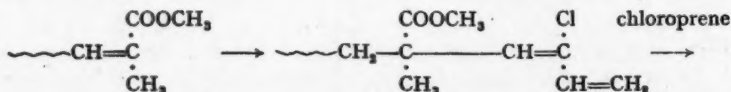


FIG. 4.—Variation of rate of polymerization as a function of the distance between the impinging beams of light.

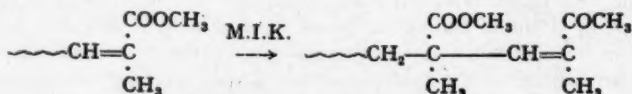
distance apart being varied. Suppose first that the beams are so far apart that the distance of the diffusion of the chains in space is much less than the separation of the beams, then the rate of polymerization due to the two beams operating together will, of course, be twice that of either acting separately. If, however, the two beams are coincident, the rate will only be  $\sqrt{2}$  times that due to either, in virtue of the operation of the square root intensity law. There will, therefore, be a gradual diminution in rate as the two beams are brought closer together, owing to the mutual interference of polymer originating in the paths of the two beams. At the mid-point in the transition curve (Figure 4) the distance through which the chains diffuse is directly obtained under these conditions. For example, in one experiment  $x=2$  cm.  $D=6$  sq. cm.-per sec. and, therefore,  $t=0.33$  sec. From the kinetic theory of gases it is possible to calculate the number of collisions with the monomer in  $t$  sec., which may be denoted by  $N_t$  and as the number of monomer units added  $N_m$  is given by the molecular weight, then the absolute collision efficiency is simply  $N_m/N_t$ . For the acrylate reaction this figure is about  $10^{-7}$ . That is, on the average, only one collision in ten million is chemically effective.

## INTERPOLYMERIZATION

As some of the major problems in polymerization reactions are only now being tackled, it would seem perhaps futile to say any thing about interpolymers. By this term is meant the incorporation of different types of unit in one and the same individual molecule. In the normal method of carrying out polymerization in the liquid phase it is sometimes rather difficult to say during the polymerization of a mixture of potentially polymerizable molecules whether true interpolymers are in fact formed. The active polymers of long life, however, provide a technique whereby true interpolymerization may be detected in a very direct fashion. For example, if live polymethacrylate is deposited on a suitable support and another molecule is brought into contact with it, then three types of behavior may be exhibited: (a) no reaction occurs at all, (b) the second molecule reacts with the active end of the methacrylate and kills the polymer, (c) the second molecule polymerizes on top of the active acrylate. It is difficult to discriminate sometimes between (a) and (b), for the number of centres is so small that the detection of the disappearance of the second molecule is not easy experimentally. The problem is, however, simply solved by bringing more methacrylate into contact with the polymer when in case (a) polymerization will proceed at undiminished velocity. But more can be done than demonstrate that one molecule will grow on top of another. For instance, if chloroprene is put into contact with live methacrylate, it will polymerize rapidly to a rubber thus:



with a substratum of polymethacrylate. If, in addition, the chloroprene is now replaced by methacrylate, the latter molecule polymerizes as rapidly as before. Thus it is possible to demonstrate that a true interpolymers of chloroprene and methyl methacrylate has been formed. In fact, in one experiment it proved possible to make a twelve-fold molecular sandwich, consisting of alternate layers of polymethacrylate and polychloroprene. It is of interest to mention that the experiment took three weeks to complete, there being continual growth night and day. The molecular length then reached the extraordinarily high value of about 1 cm. It is also possible to deposit polychloroprene photochemically and then grow molecular sandwiches on top of this polymer. Recently it has been found to be practicable to make interpolymers of methyl isopropenyl ketone and methyl methacrylate:



the former molecule growing in darkness like the other molecules mentioned above. These interpolymers behave very selectively to certain molecules. For example, oxygen will poison the polychloroprene centres, yet has no effect on the methacrylate centres, whereas ethylene, acetylene and butadiene cannot, unfortunately, be induced to polymerize by these active molecules. In fact, these molecules do not even react with the terminal double bond.

Finally, mention may be made of two less highly developed, but none the less interesting topics in connection with big molecules. The first is the question of

the distribution of molecular sizes in any synthetic polymer. By adopting kinetic methods it has been possible to work out the distribution for every type of starting and terminating mechanism met with in this kind of investigation. The position now is that some relatively simple method is required to verify such conclusions. The second problem is that of determining quantitatively the degree of cross-linking in polymers. Two methods have been attempted, but progress has been slow. One method consists of studying carefully the thermal depolymerization in a molecular still. Preliminary experiments have shown that cross-linked polymers are rather more stable than straight chain polymers, so that the velocity of depolymerization does afford a criterion of the degree of cross-linking. The technique is, however, confined to those molecules which depolymerize smoothly to monomer, without the production of large quantities of by-product.



# THE ACTION OF OZONE IN THE PHENOMENON OF THE CRACKING OF RUBBER SUBJECTED TO REPEATED MECHANICAL STRESSES \*

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Various rubber articles are subjected in ordinary service to repeated stretching, compression and cutting and to combinations of such forces. Repeated flexing is frequently encountered also. All these forces cause repeated changes, either positive or negative, in the dimensions of the outside surface of the rubber article. Among the important rubber products which undergo such stresses are tires, belts and shoe soles. The stresses to which the tread of a tire is subjected are certainly complex and variable. In this particular case, there are, in addition to the initial static tension, forces of compression, flexing and torsion. A rubber belt offers a simpler problem, for in this case it is possible to distinguish the following cycle of changes on the outside surface: a constant elongation in the taut section of the belt; a sudden increase in elongation on passing over the driving pulley, during which time a constant flexing stress (which depends on the curvature of the pulley) must be added to the tension on the belt; a decreased elongation along the surface of the belt in contact with the pulley; and finally a rapid return to the minimum value existing in the belt when under no tension. An analogous cycle of changes takes place at the driven pulley. Each element of the surface of a belt undergoes, therefore, during each complete revolution, two periods of tension, between which the element is alternately in the taut and in the slack section of the belt.

After a sufficient length of time in service, which depends on the character of the material and on the service conditions, these repeated stresses finally lead to cracking on the surface of the belt. This same effect occurs on other rubber products, especially on tires, but in this case the cracks are localized in definite zones on the outside surface, generally at the bottom of the grooves of the design, where the stresses reach their maximum values, but sometimes on the sidewalls.

This phenomenon, which becomes visible when the surface cracks enlarge to deep fissures, has been the subject of numerous laboratory investigations, particularly in connection with the use of anticracking agents and antioxidants. It is to the credit of these products that it is now possible, from a practical point of view, to confine the cracking to narrow limits, and in many cases to reduce it to negligible proportions compared to other effects in service.

It is the task of the experimenter to compare various protective agents and to rank them in their order of effectiveness in retarding the appearance and progress of surface cracks, and to study the mechanism of the action of these agents.

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\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Gomma*, Vol. 4, No. 1, Pages 1-6, January-February 1940.

Let us review briefly the various testing methods which have been developed to study, on a laboratory scale and with small test-specimens, the behavior of rubber subjected to repeated stresses. Some of these methods have been utilized in an attempt at unification by the American Society for Testing Materials (A.S.T.M. Designation D430-35T), and this in itself is an indication of the widespread interest and importance now shown in tests of this kind.

In some of the machines, the test-specimen is held by its ends in two clamps or jaws, one of which has a reciprocating motion, so that the specimen is subjected to simple tension. In this group may be mentioned the De Mattia flexing machine<sup>1</sup> and the Firestone flex-cracking machine<sup>2</sup>, both of which use straight test-specimens, and the Schopper testing machine, which requires ring test-specimens. The first of these three machines is undoubtedly the most widely used. Various investigators have employed machines of similar character, and the only substantial differences have been the forms of the test-specimens and the conditions of stressing, *e. g.*, minimum tension, and amplitude and frequency of the stress-cycle.

In simple tension tests, the stresses are almost always continued until rupture occurs, and the time, *i. e.*, the number of cycles, required to rupture the test-specimen is measured. In such tests, the stresses are localized and increase with increase in the depth of the cracks, so that usually one of the fissures finally become so extensive that rupture of the test-specimen occurs. Hence only by determining the average time required to rupture a large number of samples is it possible to make comparative tests.

Other machines have been constructed to flex test-specimens repeatedly. In these tests cracking always takes place in the stretched section. Such machines can be divided into two types. In one case the test-specimen (or series of test-specimens) has the form of an endless band which travels on two or more pulleys, one of which drives the mechanism. To this group belong the du Pont flexing machine<sup>3</sup> and the Pirelli machine<sup>4</sup>. In the second type, a parallelpiped-shaped test-specimen, usually with one or more transverse grooves or channels, is subjected to repeated flexing under various conditions. To this group belong the flexing machine of the India Tire and Rubber Co. and other machines derived from this machine<sup>5</sup>.

Insofar as the conditions under which the sample is stressed are concerned, the Scott flexing machine<sup>6</sup>, although generally used for measuring the tendency of fabric plies to separate, belongs to the first type; the so-called bend-flexing test<sup>7</sup>, which is carried out on a De Mattia machine, belongs to the second type.

The laboratory of the Pirelli Company is equipped with most of these testing machines, and they have been tested comparatively by numerous rigorously controlled experiments, using a vulcanizate of the automobile tire-tread type, containing 45 per cent of gas black (based on the rubber content) and no anti-cracking agent, and also using twelve more vulcanizates prepared from the same recipe but with the addition to each of the twelve of 1 per cent (based on the rubber content) of a different antioxidant or anticracking agent.

In tests in connection with the attempts at unification by the American Society for Testing Materials (*loc. cit.*), the specifications were followed scrupulously.

The results of the completed work can be summarized as follows.

(1) The method of preparation of the test-specimen plays a part in every test which involves repeated flexing. In addition, mixing, vulcanization and age of the test-specimens influence the results. The conditions of preparation and storage of the samples are especially important, *e. g.*, the smoothness of

the sample, the condition of the cutting die, the conditions under which the test-specimens are kept, etc.

(2) All the testing methods are influenced by atmospheric conditions, including temperature, humidity and ventilation.

(3) All the testing methods have the disadvantage of giving extremely variable results, and therefore they must always be carried out under strictly comparable conditions and always with a large number of test-specimens.

(4) In spite of these facts, it has been possible to obtain results from which various products can be ranked in groups according to quality. However, within each group, it is practically impossible to rank the individual products in their order of quality. In other words, the testing methods show only relatively large differences, and it is from this point of view alone that the various methods may be said to be comparable.

A comparison of the relative qualities obtained by the various methods shows considerable disagreement. In some cases exactly the opposite results were obtained, and these were confirmed by repeated tests.

In view of these facts, which seemed to merit particular investigation, we were encouraged to improve the methods of experimentation, to study the various factors which play a part in the phenomenon of cracking by repeated stressing, to attempt to differentiate these factors, and finally to examine them individually.

Thus, tests were carried out to establish the influence of dimensional factors, an influence which may explain the differences in the results obtained with the various testing methods. To a certain extent these experiments were a repetition of work by other investigators. It was, for example, proved that the life of a sample depends on the amplitude of the cycle, *i. e.*, the greater the cycle the shorter the time required for cracks to appear. This confirms the results obtained by Cooper<sup>2</sup>.

We have been able to prove, both with ring test-specimens in the Pirelli machine and with trapezoidal strips in a machine of the De Mattia type, that the deepest cracks correspond to a minimum elongation of approximately 10 per cent. This value, which is of the same magnitude as the critical elongation of rubber exposed to light and to ozone<sup>8,9</sup>, led to part of the present investigation being devoted to a study of this particular point.

It was found that, by increasing the minimum elongation above a definite limit, the span of life of the rubber increased enormously. A ring stretched 75 per cent showed no visible changes after flexing for 12 days, whereas when stretched only 20 per cent it was badly deteriorated after 24 hours. This phenomenon has already been described by other investigators.

The next step was an improved means of observing the test-specimens, particularly in the early stages of the test. This was accomplished by recourse to microscopic examination, with a magnification of 80, instead of examination by the naked eye.

It may be of interest at this point to describe briefly the character and the distribution of the cracks which were observed by this means. After the rubber had been stressed sufficiently long, there appeared on the one hand numerous tiny cracks not always visible to the naked eye, which were distributed uniformly over the surface and, on the other hand, relatively large, deep fissures, which were few in number and were distributed irregularly. The orientation of all these cracks and fissures was at right angles to the direction of elongation. Occasional exceptions to this were due chiefly to irregularities on the surface of the test-specimen, *e. g.*, marks made on the specimen.

Evidence seemed to show that, in general, although not always, small cracks appear before fissures are formed. Probably the small cracks are attributable to some external influence which causes attack of the entire surface of the test-specimen.

When various facts, such as the electrification of samples subjected to repeated mechanical stresses, the existence of a minimum critical elongation, the great resistance to flexing at a rather high minimum elongation and the appearance of cracks consistently as a surface effect, are considered together, one is led to the conclusion that these uniformly distributed cracks are caused by ozone.

Neal and Northam<sup>10</sup> considered the possibility of the concomitant action of air and of ozone, without, however, succeeding in detecting the presence of ozone; at least their work led them to the conclusion that ozone plays no part in the phenomenon. Furthermore, in a publication of Berliner<sup>11</sup>, mention is made of a method for accelerating mechanical tests, which involved exposure of test-specimens to ozone until a predetermined degree of cracking was reached. This choice of preliminary treatment could not have been accidental.

In view of all this, stretched test-specimens were exposed to an atmosphere containing ozone. In a parallel series, tests were carried out with rings on the Pirelli machine and with straight test-specimens on the De Mattia machine, using in each case the series of vulcanizates mentioned above. However, in the tests in ozone, the conditions employed by other investigators, *e. g.*, Williams<sup>8</sup>, Haushalter, Jones and Schade<sup>12</sup>, Somerville, Ball and Cope<sup>9</sup>, Kearsley<sup>13</sup> and Neal and Northam<sup>10</sup>, were modified to the extent that the concentration of ozone was diminished to about 1:1,000,000 so that the time of the tests would be of the same general order as that of the mechanical tests. It was felt that too severe an attack on the surface of the test-specimens would alter the mode of action of the antioxidant or anticracking agent and obstruct its effectiveness; in fact the concentration and consequent migration must certainly play a part in the mechanism of the action of these agents. If the phenomenon proceeds too rapidly, migration, which is relatively slow, plays a minor rôle. The thin surface film, deprived beforehand by the action of ozone of a part of its antioxidant, which cannot be renewed promptly, is the first to be destroyed. Consequently, the relative effectiveness of various protective agents will be changed in favor of those which migrate rapidly<sup>14</sup>, even if they are relatively ineffective otherwise.

Furthermore, a slow test makes it possible to make more measurements during the progress of the changes which take place, and to distinguish with a greater degree of exactitude the formation of cracks.

In the tests involving exposure to ozone, the apparatus shown in Figure 7 was employed. A current of compressed air, regulated by a suitable reduction valve, passed through a desiccator containing calcium chloride and thence through a diaphragm flowmeter. At the outlet of the latter, part of the air passed directly into the chamber in which the samples were exposed, while more air passed through a second flowmeter with a porous diaphragm into an ordinary ozonizer with dark discharge (*scarica oscura*) and designed for therapeutic use.

Before entering the chamber containing the samples, the current of ozonized air was mixed with the other air current. In this chamber, which had the form of a vertical cylinder, was a plate with seven holes, which distributed the air over the cross-sectional area. A tube mounted on the top of the chamber served as an outlet for the current of air.

The desired dilution of ozone was obtained by regulating the volume of air which passed through the ozonizer with respect to the total volume (7 mc. per



hour) and regulating the formation of ozone by varying the voltage applied to the ozonizer.

The formation of ozone was controlled by collecting a definite volume of ozonized air at the outlet of the ozonizer and determining its ozone content. Periodic control measurements showed that the ozone content did not vary greatly when the flow of air and the voltage of the ozonizer were maintained constant<sup>15</sup>. The effect of a variation of the concentration of ozone on the span of life of the exposed rubber samples was, however, anything but negligible as far as the actual times for cracks to appear were concerned. For this reason all tests were carried out under rigidly controlled and directly comparable conditions. However, relative results are of the most interest, and it is also possible to carry out successive series of tests, provided that a control sample is always used in each series.

Samples exposed to ozone (strips at various elongations from 0 per cent to 100 per cent), samples stressed repeatedly on a De Mattia machine (the test-

TABLE I

Antiscorching agent	Ozone	Time for cracks to appear (in hours)	
		Pirelli machine	De Mattia machine
None .....	15	8	12
A .....	17	9	13
0.5A + 0.5E .....	20	13	15
B .....	20	13	16
C .....	24	18	20
D .....	26	18	21
E .....	30	24	24
F .....	34	27	28
G .....	34	28	28
H .....	38	30	32
I .....	45	34	38
L .....	50	38	43

specimens were identical to those exposed to ozone and to straight test-specimens of type B of the American Society for Testing Materials, tested at a minimum elongation of 20 per cent and maximum elongation of 100 per cent), and finally ring specimens tested on a Pirelli machine were examined at brief intervals microscopically with a magnification of 80. Table I gives the elapsed times for the first signs of cracking to appear microscopically. Each of the times recorded is the average of at least three individual tests, and the deviations in the values were never greater than 10 per cent.

The obvious parallelism between the three methods of testing might in itself be regarded as confirming evidence that a common cause is involved in the two cases, *i. e.*, cracking by exposure to ozone and by flexing. It might be objected that resistance to the action of ozone and to mechanical stress may decrease at about the same rate, but the identical appearance of the cracks formed by ozone and by flexing, respectively, is sufficient evidence to outweigh this objection.

Figures 1 to 4 represent four photomicrographs of cracking under different conditions. Figures 1 and 2 show two test-specimens of the du Pont type (American Society for Testing Materials); the first was flexed on a machine of the du Pont type; the second was exposed, while elongated, to ozonized air. Figures 3 and 4 show straight test-specimens of the De Mattia type, one of which was tested in the machine, the other of which was exposed to ozone. The first



ones were vulcanized in a press and show traces of the tool marks on the press; the second ones were vulcanized between sheets of laminated metal and show the striations of the lamination process.

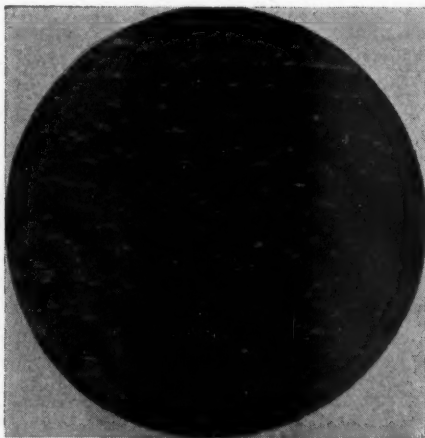


FIG. 1.—Photomicrograph of the surface of a test-specimen after having been subjected to repeated flexings on a flexing machine of the du Pont type. (Magnification 80.)

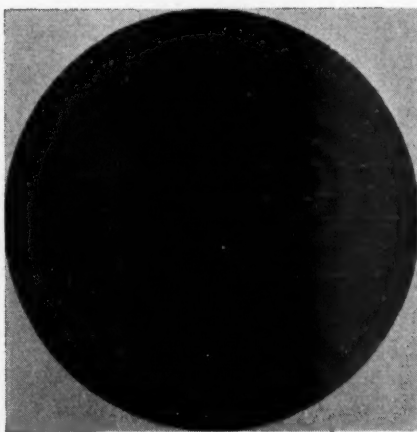


FIG. 2.—Photomicrograph of the surface of a test-specimen of the du Pont type after exposure to ozone.

Nevertheless, the appearance and the distribution of the cracks is absolutely identical in the two cases, and this is further confirmation of the hypothesis just advanced.

It seemed desirable to confirm the presence of ozone during the tests. The extremely low concentrations of ozone and its rapid reaction with the rubber, in the proximity of which the ozone should be formed, made it impossible to

detect it by ordinary means. Even Neal and Northam<sup>10</sup> were unsuccessful in establishing its presence by placing small strips of stretched rubber very close to the test-specimens. Recourse was therefore had in the present work to a

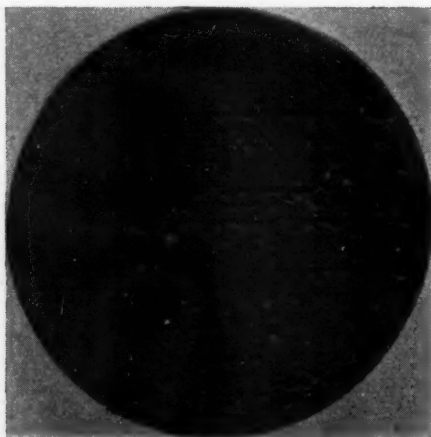


FIG. 3.—Photomicrograph of the surface of a test-specimen after having been subjected to repeated stresses on a machine of the De Mattia type.

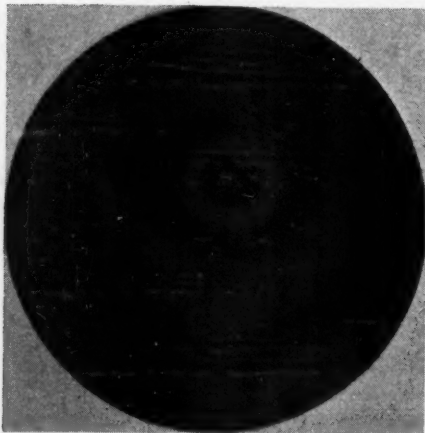


FIG. 4.—Photomicrograph of the surface of a test-specimen of the De Mattia type after exposure to ozone.

different method, *i. e.*, a substance was incorporated in the rubber to detect the presence of ozone. Tetramethyldiaminodiphenylmethane, which turns yellow in the presence of ozone, was added to a white rubber stock, and vulcanized rings were prepared from this stock and from a corresponding stock containing no tetramethyldiaminodiphenylmethane; also a ring was made in two sections of the vulcanizates with and without tetramethyldiaminodiphenylmethane.

After 24 hours' flexing on the Pirelli machine, the ring containing tetramethyldiaminodiphenylmethane and the section of the composite ring which contained the same reagent had turned light yellow.

Another test which seemed to be very significant was the following. A special laboratory apparatus was constructed in such a way that a vulcanized ring revolved and at the same time was squeezed between an annular channel, the inside wall of which was the outside periphery of a fixed disc, and the outside wall of which was the inside surface of a rotating pulley. This construction is more evident in Figure 5.

The outside surface of the rubber ring, which was stretched while being flexed, was therefore in contact with the metal walls except at the moment of



FIG. 5.—Apparatus used for flexing tests while electrically grounded and while insulated.

flexing. The testing procedure consisted in revolving separately identical rings while the machine was grounded electrically and while it was insulated. Only the electrostatic conditions were varied.

After equal times of testing, the rings which had been on the machine while it was insulated were in noticeably better condition than the corresponding rings which had been on the machine while it was grounded electrically. This is further proof of the importance of the electrical factor. Figure 6 shows clearly the different appearance of the rings tested under these two different conditions.

The hypothesis which has been advanced can be put to various other tests. A more thorough investigation of the electrical phenomenon, tests in various media, etc., might be of further aid in explaining the phenomena. However, it seems already clearly demonstrated that ozone plays an important part in tests of the kind described in the present work.

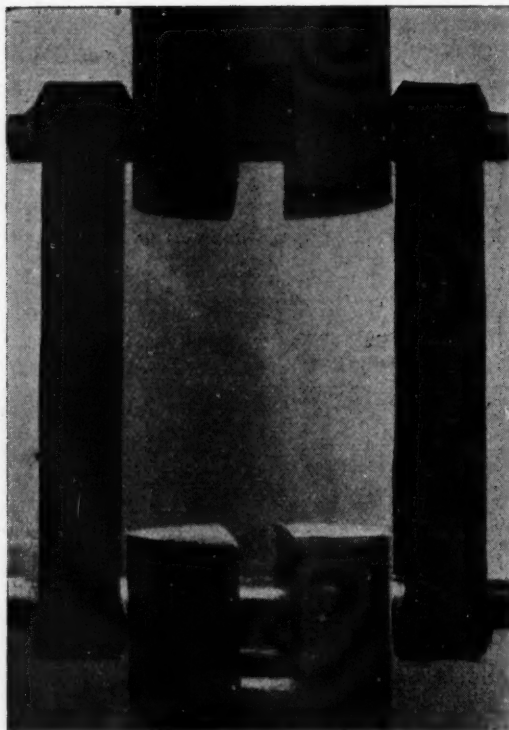


FIG. 6.—Rings tested on the machine shown in Figure 5. The test-specimen at the right was tested with the apparatus electrically grounded; the test-specimen at the left with the apparatus insulated.

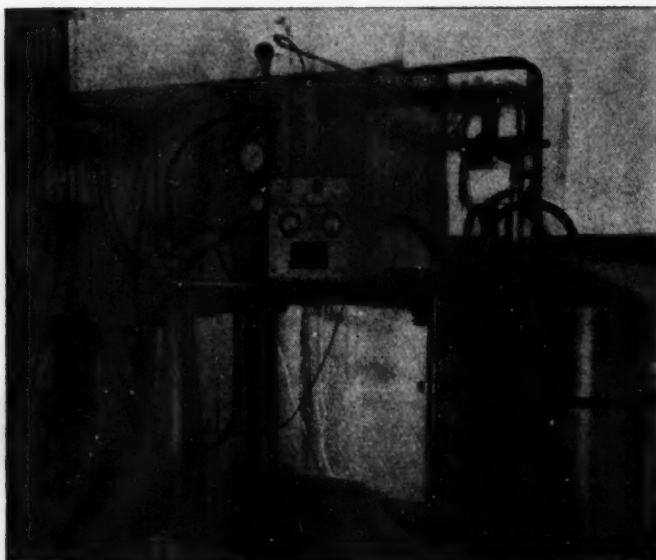


FIG. 7.—Apparatus used for tests in ozone at low concentration (1:1,000,000).

## ACKNOWLEDGMENT

The investigation was carried out in the physical laboratory of the Pirelli Company of Italy, with the collaboration of Gioacchino Ricca, to whom is due credit for the photographs and photomicrographs.

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- <sup>3</sup> *Rubber Age* (N. Y.) **26**, 542 (1930).
- <sup>4</sup> A rubber ring, vulcanized in a press, was mounted, in the form of a stretched belt on two pulleys, one of which (the driver) was 30 mm. in diameter, with r.p.m. of 1200; the other of which was 15 mm. in diameter. The distance between the pulleys could be varied within fairly wide limits. Originally the cross-section of the ring was rectangular; at present a ring with triangular cross-section (height 10 mm., mean diameter 150 mm.) is used.
- <sup>5</sup> Booth, *India Rubber World* **82**, No. 6, 53 (1930); Terrance and Peterson, *India Rubber World* **80**, No. 4, 62 (1929).
- <sup>6</sup> Sturtevant, "Vanderbilt Handbook", 1932, p. 51.
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- <sup>8</sup> Williams, *Ind. Eng. Chem.* **18**, 367 (1926).
- <sup>9</sup> Somerville, Ball and Cope, *Rubber Age* (N. Y.) **26**, 255 (1929); *RUBBER CHEM. TECH.* **3**, 131 (1930).
- <sup>10</sup> Neal and Northam, *Ind. Eng. Chem.* **23**, 1449 (1931); *RUBBER CHEM. TECH.* **5**, 90 (1932).
- <sup>11</sup> Berliner, "Latest World Developments in the Manufacture of Tires", New York, p. 10.
- <sup>12</sup> Haushalter, Jones and Schade, *Ind. Eng. Chem.* **20**, 300 (1928); *RUBBER CHEM. TECH.* **1**, 120 (1928).
- <sup>13</sup> Kearsley, *Rubber Age* (N. Y.) **27**, 649 (1930); *RUBBER CHEM. TECH.* **4**, 13 (1931).
- <sup>14</sup> Tests now in progress at the Pirelli laboratories have shown that this is true to different extents with different products.
- <sup>15</sup> By improving the method for drying the air and controlling the temperature of the air and the temperature of the ozonizer, it will be possible to obtain more nearly constant results.



# ACTION OF OZONE ON RUBBER AND OTHER MATERIALS \*

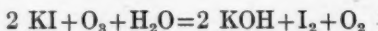
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Since the deterioration of rubber by corona discharge and by light may be related to ozone formation, it seemed of interest to study the action of ozone alone. It was soon found that the dominant factors were ozone concentration, time of exposure, and mechanical stress on the rubber. This effect of tension was noted by Haushalter<sup>1</sup>, who was making corona tests with stretched rubber. Williams<sup>2</sup>, in studying the oxidation of rubber exposed to light, found that light can produce checking or cracking, probably by the formation of a small amount of ozone. The surface deterioration of rubber in sunlight under different mechanical stresses was studied by Depew<sup>3</sup>.

In the present investigation the action of ozone on rubber compositions, not exposed to direct light but under tension and compression, was studied by placing the specimens one at a time in a box  $2\frac{1}{2} \times 3\frac{1}{2} \times 15$  inches, through which a stream of ozonized air or oxygen was passed. The box had glass sides to enable the action on the specimen to be observed.

Most of the tests were made with ordinary rubber electrical insulating tape, which has a rubber content of about 70 per cent by volume. This was cut into standard dumbbell shape 4.75 in. long, with a cross-section 0.028 by 0.25 inch. (The narrow portion formed 1.25 inches of the total length.) The stress is calculated on the original cross-section. Its tensile strength was 1140 lbs. per sq. in. at 650 per cent elongation. The ozone concentration in the box was determined by tests of the inlet and outlet air, and these were checked. Analysis was made by absorbing a known volume of the gas in a 7 per cent KI—1 per cent KOH solution. After the ozone had been absorbed (this action was extremely rapid), the solution was just acidified with  $\text{H}_2\text{SO}_4$  and the iodine liberated by the ozone in the reaction:



was titrated with 0.1 *N* sodium thiosulfate.

The ozone was generated by a water-cooled ozonizer tube. This could give up to 4 per cent ozone by volume (75.5 mg. per liter). The rate of flow was 9.6 liters per minute. Since the box holding the specimen had a volume of 2.1 liters, there were about 4.5 complete changes of ozonized air in the box per minute.

The mode of conducting the tension tests in ozone was first to clamp the upper end of the rubber strip and hang a weight on the lower end. The box was then closed and the ozonized air started through it. The time taken for the strip to break (and the weight to fall) was determined for various stresses and ozone concentrations. It is recognized that this method of testing a rubber sample under constant stress by suspending a weight on it is not representative of many actual service conditions. For example, a life test of corona-resisting rubber cable under service conditions should include a test with a sharp 90-degree bend. In such instances corona-resistant compounds will assume a per-

\* Reprinted from the *General Electric Review*, Vol. 43, No. 2, pages 93-95, February 1940.

manent set, with a corresponding decrease in stress which is very difficult to calculate.

The results are presented by the curves in Figure 1 on a linear scale and on a log-log scale in Figure 2. It is of interest to note that the time to rupture de-

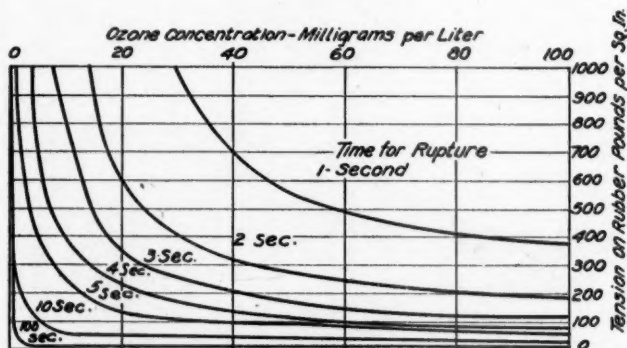


FIG. 1.—Effect of ozone on rubber under stress. Test piece, semicured rubber; standard dumbbell shape; cross section 0.028 by 25 in.

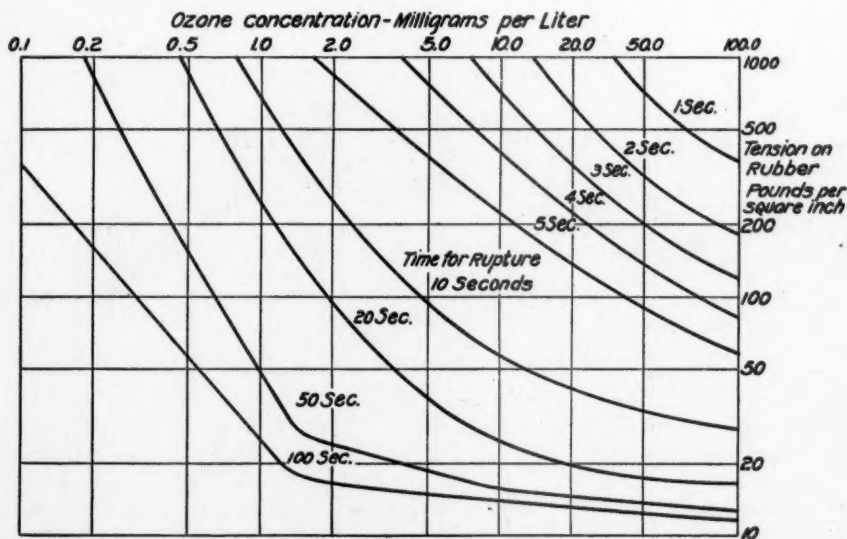


FIG. 2.—Effect of ozone on rubber under stress. Test piece, semicured rubber; standard dumbbell shape; cross section 0.028 by 25 in.

pends on both stress and on ozone concentration. At very low stress, a very long time is required for the ozone to show any effect on the rubber; and presumably if zero stress could be obtained, the ozone would be without effect on the rubber.

Various compositions of rubber were tested, including corona-resisting rubber, tellurium-cured rubber, deproteinized rubber, and sheet rubber of different de-

degrees of cure. All showed attack by ozone, to a greater or lesser extent. Corona-resisting rubber was the best in these comparative tests. However, it is difficult to extrapolate to actual service conditions, since the success of corona-resisting rubber insulation depends on its low modulus and high permanent set, and, as previously mentioned, the consequent decrease in stress leads to much longer life in a given ozone concentration.

Hard-rubber sheet, 20 mils thick, stressed by being bent and put into the ozone, broke at the point of maximum stress in 15 seconds.

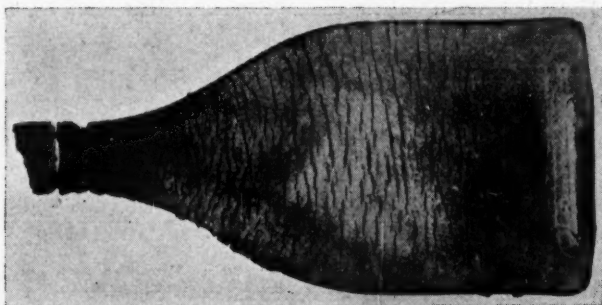


FIG. 3.—Sheet rubber which has failed under tension and exposure to ozone.



FIG. 4.—Block of rubber which has been stressed by bending and exposure to ozone.

Synthetic materials which showed no evidence of ozone attack, either stressed or unstressed, were alkyd, phenolic and vinyl synthetic resins, and cellulose acetate.

During the action of concentrated ozone (44.5 mg. per liter) the stressed rubber became warm. Rubber tape was wrapped around a thermometer bulb, the wrapping giving tensile stress. The temperature rose from 32 to 39 C in 30 seconds, when the rubber, disintegrating, fell away from the bulb.

The form of attack of ozone on rubber under tension is characteristic. Tiny cracks form, always at right angles to the direction of stress. The curved stress lines can be recognized in Figure 3, where failure has occurred in the more highly stressed portion.

Figure 4 shows the type of failure of a bent rubber bar  $\frac{1}{2} \times \frac{1}{2} \times 2$  inch, having tensile stress on the upper side. Figure 5 shows a top view of the bar.

In a stretched specimen, failure is generally initiated from one of the little nicks on the edge started by ozone attack. If tension is uniform in all directions, as rubber stretched over a ball, failure starts as a reticular network. It looks like dried mud, but the five- or six-sided figures observed on a mud flat were not observed in the test of rubber.



FIG. 5.—Rubber (top view of specimen in Fig. 4) which has failed under bending and exposure to ozone.

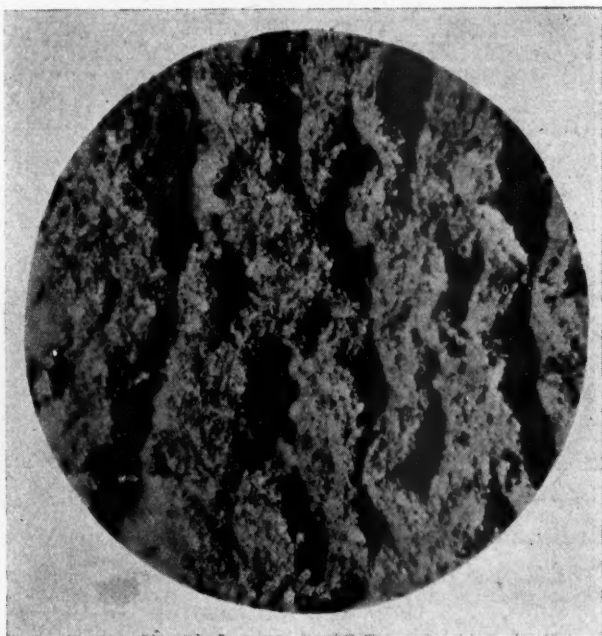


FIG. 6.—Photomicrograph ( $\times 25$ ) of stretched rubber which has been exposed to ozone.

The initial stage of attack can be observed under the microscope, at 130-diameter magnification. Tiny round pinholes appear, then become isolated cracks at right angles to the tension. These then enlarge and interlace as shown in Figures 3 and 6, leading to final rupture.

The rather different type of attack on deproteinized rubber is shown in Figure 7.

It was found that accelerated attack on rubber by ozone is also caused when the rubber is under pure compressive, as well as tensile, stresses.

This is rather difficult to observe, because exposed portions of the specimen under tension disintegrate first. Satisfactory observation, however, was made as follows. A bar of rubber  $\frac{1}{2} \times \frac{1}{2} \times 2$  inch was bent and held by a metal frame. All of the rubber was coated with Glyptal varnish, except a small square on the interior of the bend. This is the one region under pure compression. The remainder of the bar, at the clamped ends, the neutral axis, and the top which was under tension, were all protected from ozone by the Glyptal.

Under these conditions, it was found that the compressed portion was more rapidly attacked by ozone than was a nearby unstressed bar. The rubber ap-

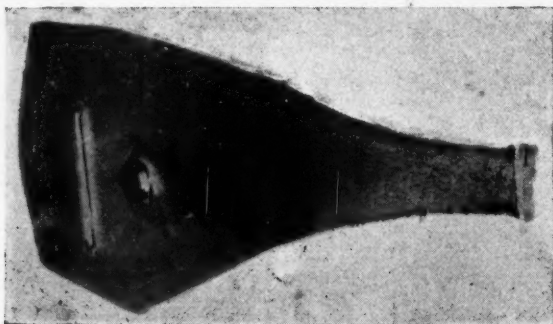


FIG. 7.—Deproteinized rubber which has failed under tension and exposure to ozone.

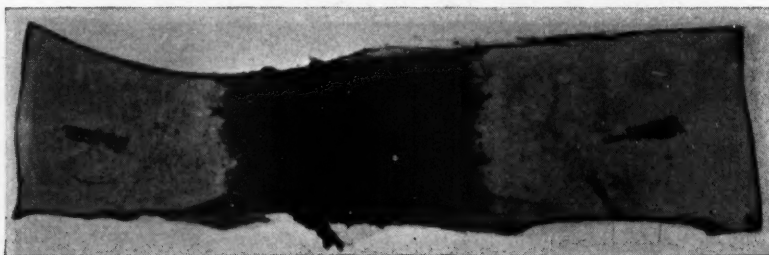


FIG. 8.—Rubber which is failing under compression and exposure to ozone.

peared to sprout above the compressed surface as a black feathery disintegration product where the ozone attack occurred. Figure 8 shows the appearance of the formation.

From this work it is apparent that attack by ozone is reduced by reduction in mechanical stress. This was taken advantage of in the design of a connection from glass to rubber tubing. The conventional joint, Figure 9(a), produces a high stress in the rubber at the point of emergence from the glass tube. If the glass is necked down to the inner diameter of the rubber tube and extended into it as in Figure 9(b), the point of high stress in the rubber is removed from the neighborhood of the ozone and is protected by the glass. Hence, the rubber tube lasts much longer. It is still better of course to use a tube of Glyptal, for this material is unaffected by ozone.



This investigation may then be summarized as follows. Various rubber compositions were tested in ozone of varying concentrations by hanging a weight on a test strip to give a constant known stress, and the time for the strip to break was measured. It was found that at high stresses, even low ozone concentrations result in short life of the rubber, whereas at very low stresses even high ozone concentrations do not affect this material.

Rubber is rapidly attacked when under tension or compression. Though attacked to different degrees, hard rubber, corona-resisting rubber, deproteinized

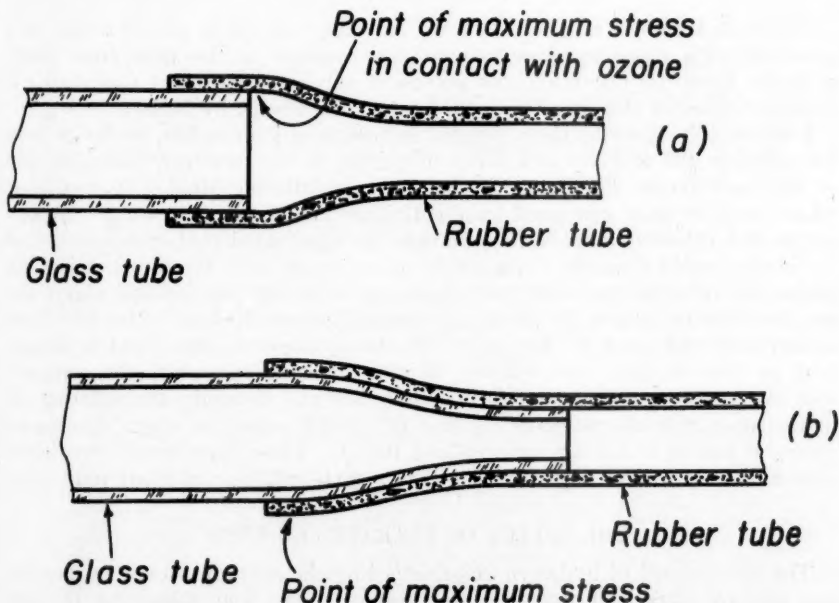


FIG. 9.—(a) Conventional type of glass to rubber tube connection, which accelerates the disintegration of the rubber tube at its junction with the glass tube when used to conduct ozone. (b) Special type of connection designed to eliminate the objectionable structural feature present in ordinary design.

rubber, and tellurium-cured rubber showed the same general type of relations between stress, ozone concentration, and time to rupture. Alkyd, phenolic and vinyl synthetic resins and cellulose acetate, whether stressed or unstressed, gave no evidence of attack by ozone.

From this research it is evident that, to specify the life of a rubber composition, the mechanical stress as well as the ozone concentration in the surrounding atmosphere must be known.

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# THE STABILITY OF CHLORINATED RUBBER AND ITS FRACTIONS \*

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## INTRODUCTION

Chlorinated rubber has been introduced extensively as a raw material and especially as a distinctive raw material for lacquer; at the same time fairly extensive literature on this highly polymeric substance has been published. A valuable review of this literature is to be found in a work by Nielsen<sup>1</sup>.

Ever since it was first manufactured in commercial quantities, we have been interested in the stability and other properties of this new raw material, and at the very outset Fol and Bijl<sup>2</sup> of the Internationale Rubber Vereeniging, whose work is being continued by the Rubber Foundation, carried out experiments with chlorinated rubber. Meanwhile the chlorinated rubber manufactured by various world concerns as an article of commerce on a large scale has fully proved its *raison d'être*, while the arguments originally put forward about the new material because of its chemical composition (see Nielsen<sup>1</sup>, page 67) have scarcely affected these developments. We have, however, considered it important, in view of these developments, to determine experimentally the composition of ordinary commercial chlorinated rubber and to study the splitting off of hydrogen chloride, which is set free in minute quantities when chlorinated rubber is heated to a temperature above 100° C. These experiments were commenced in September 1934, but the results could not be published until now.

## THE EFFECT OF ULTRAVIOLET RAYS

The splitting off of hydrogen chloride is brought about not only by heating but also by ultraviolet rays (not by visible light). The absorption of light with a wave length of less than 3000 Å is extremely intensive (see Nielsen, page 49); as the absorption of light is the actual cause of the decomposition of the chlorinated rubber, it may be expected that the effect of ultraviolet rays on a layer of chlorinated rubber will be restricted to the surface layers. This is actually the case, as will be gathered from the following.

By immersing strips of copper in a 20% solution of chlorinated rubber in benzene and allowing them to drain and dry in a vertical position, we covered them with a layer which was thinner at the upper end than at the lower. When subjected to ultraviolet rays<sup>3</sup>, the copper began to show signs of discoloration, where the layer of chlorinated rubber was thinnest, after 3.5 hours; in other places discoloration occurred later or not at all during 9 hours' treatment.

It is noteworthy that a strip of copper only partially covered with chlorinated rubber becomes most discolored on the plain, uncovered surface, and in particular on that section which is immediately above the chlorinated rubber layer when the ultraviolet rays are applied. The plain surface of the copper immediately below the chlorinated rubber layer does not discolor at all. Discoloration of the section of the copper above the chlorinated rubber commences after an irradiation of only 10 minutes.

\* Reprinted from the *Communications of the Rubber Foundation*, Amsterdam, No. 14, pages 7-30, September 1939.

This might be accounted for by the fact that the hydrogen chloride which originates in the surface layer of the chlorinated rubber film when ultraviolet rays are applied cannot penetrate through the film to the surface of the copper; it consequently emerges from the chlorinated rubber and is carried away by the air current which rises along the copper strips when the ultraviolet rays are applied and which passes over the unprotected surface of the copper<sup>4</sup>.

Seeing therefore that the photochemical decomposition of chlorinated rubber is greatly influenced by the specific surface of the matter to be tested, we did not choose this reaction for determining the stability of chlorinated rubber specimens.

#### THERMAL DECOMPOSITION OF CHLORINATED RUBBER

The decomposition of chlorinated rubber when heated, both dry and in water, was further studied. To this end we had at our disposal eight technical chlorinated rubber specimens from four German manufacturers (A-D). Of A and B we had specimens with three different degrees of viscosity: 1 (low), 2 (medium), 3 (high).

##### (a) Heating without water:

It was decided to begin with the dry heating of a specimen A<sub>2</sub>. About 10 grams of pulverized chlorinated rubber were weighed, placed in a U-tube and heated for 722 hours in a thermostat at  $100 \pm 1^\circ \text{C}$ . A slow continuous stream

TABLE I  
DRY HEATING OF CHLORINATED RUBBER AT 100, 130 AND 150° C (SPECIMEN A<sub>2</sub>)

Temperature	Duration of heating (hrs.)	% Cl split off as HCl	% Cl split off in total	Loss of weight (%)	Loss of weight Loss of chloride
$100^\circ \pm 1^\circ \text{C}$	722	0.21	0.24	5.03 <sup>a</sup>	21
$130^\circ \pm 2^\circ \text{C}$	14½	0.45	0.44	6.4	14.5
$150^\circ \pm 4^\circ \text{C}$	1½	—	0.29	7.6	26.4

of nitrogen was passed through the U-tube and the hydrogen chloride formed was collected in water<sup>5</sup> and neutralized with 0.025 *N* alkali. The gas flowing out of the absorption vessel on the first days had a distinct odor of  $\text{CCl}_4$ . At the end of the heating, the total chloride collected in the absorption vessel was determined by the Mohr titration. While a total of 0.61 millimol of acid had been titrated, there was found to be 0.68 millimol of chloride. Accordingly, in addition to HCl, also basic reacting gases were emitted from the chlorinated rubber.

The experiment was repeated with specimen A<sub>2</sub> at  $130^\circ$  and at  $150^\circ \text{C}$ . The results obtained are given in Table I and Figure 1.

From the figures in the last column of the above table it will be evident that there is no connection between loss of weight and loss of chlorine. It is probable that the loss of weight is in the main due to escape of the solvent ( $\text{CCl}_4$ ) incorporated in the chlorinated rubber. A number of important conclusions may however be drawn from the curves.

In the first place the curves should make it possible to determine the quantity of decomposed chlorinated rubber if the splitting off of chlorine is a monomolecular reaction. In this case we are to apply:

$$(1) \quad -dc/dt = K \times c$$

(where  $K$  is the velocity constant,  $c$  the unknown quantity of decomposed chlorinated rubber, and  $dc/dt$  the rate of reaction, which is to be read from the curve.

We now take two different points of the decomposition curve. Let here the split-off quantities of chlorine be  $Z_1$  and  $Z_2$ ; the slope of the tangents at the curve in these points is then:

$$(2) \quad -(dc/dt)_1 = K \times (C_0 - Z_1)$$

$$(3) \quad -(dc/dt)_2 = K \times (C_0 - Z_2)$$

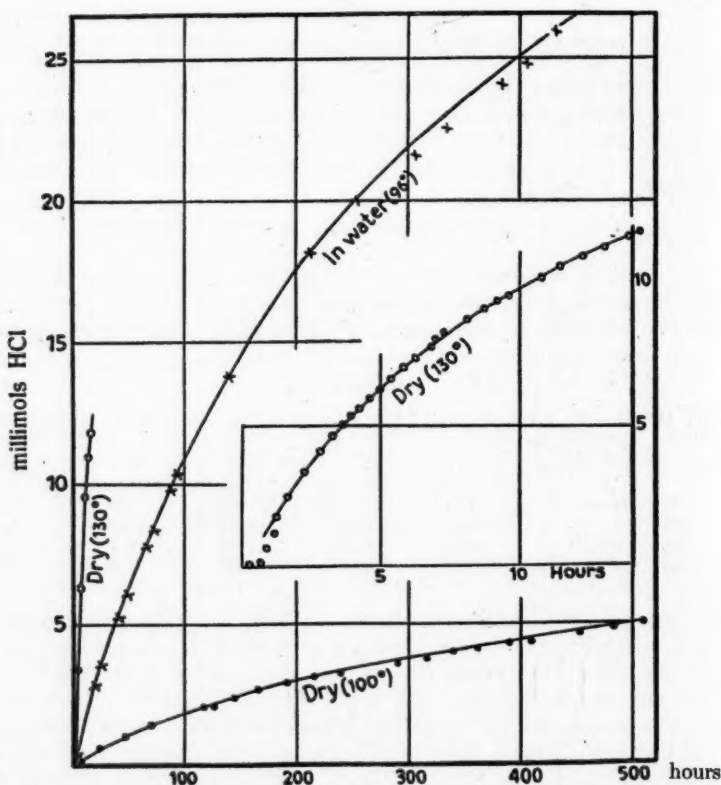


FIG. 1.—Amount of hydrogen chloride split off when chlorinated rubber is heated (Specimen  $A_2$ ).

where  $C_0$  is the maximum separable quantity of chlorine which can be split off present before the heating process. This quantity is therefore a measure of the portion of decomposable substances in chlorinated rubber. We eliminate  $K$  from (2) and (3):

$$\frac{(dc/dt)_1}{(dc/dt)_2} = \frac{C_0 - Z_1}{C_0 - Z_2} \text{ and dissolve from it the unknown } C_0.$$

$$(4) \quad C_0 = \frac{(Z_2 - Z_1)(dc/dt)_2}{[(dc/dt)_1 - (dc/dt)_2]} + Z_2$$

If we apply this analysis to more pairs of points on the same curve, we must always obtain the same value for  $C_0$ ; if this is not so, the reaction is either not a monomolecular one or there are more monomolecular reactions going on at the same time.

Before we give an exemplifying calculation, it must be pointed out that, since the experiments were not carried out with a high degree of exactitude, the calculation cannot be expected to lead to very concordant values of  $C_0$ .

For dry heating at 100° C, we obtain the following figures:

$$\text{Formula (4a)} = \frac{(Z_{700} - Z_n)(dc/dt)_{700}}{[(dc/dt)_n - (dc/dt)_{700}]} + Z_{700}$$

The maximum quantity of chlorine which can be split off at these temperatures is therefore only very small compared with the total quantity of 65%

TABLE II

CALCULATION OF THE MAXIMUM AMOUNT OF CHLORINE WHICH CAN BE SPLIT OFF BY DRY HEATING AT 100° C (SPECIMEN A<sub>1</sub>)

Duration of heating in hours	100	200	300	400	500	600	700
Amount of chlorine ( $Z_n$ ) split off (in %) .....	0.067	0.109	0.135	0.157	0.183	0.209	0.228
Rate of decomposition $(dc/dt)_n$ 90/100 hrs. ....	0.0486	0.0299	0.0262	0.0243	0.0224	0.0217	0.0202
$Z_{700} - Z_n$ .....	0.161	0.120	0.094	0.071	0.045	0.0186	—
$(dc/dt)_n - (dc/dt)_{700}$ .....	0.0277	0.0090	0.0052	0.00355	0.00149	0.00073	—
$C_0$ calculated in % according to Formula (4a) .....	0.35	0.51	0.60	0.67	0.86	0.76	—

TABLE III

CALCULATED MAXIMUM QUANTITY (IN PERCENTAGE) OF SEPARABLE CHLORINE WHICH CAN BE SPLIT OFF WHEN HEATED AT 130° C, SPECIMEN A<sub>2</sub>

Calculated from the values of $Z_n$ and $(dc/dt)_n$ , after 14 hours heating and	2½ h.	3 h.	5 h.	9 h.	11 h.
$C_0$ (in %) .....	0.57	0.60	0.61	0.64	0.66

of chlorine present. The calculation of the portion which can be split off does not give constant values; the average amounts to about 0.63% (Table II).

Decomposition at 130° yields more concordant results (Table III).

Here the constancy of  $C_0$  is very satisfactory. Moreover, it follows from this that  $C_0$  has the same value at 130° C as at 100° C. We may therefore assume that in all probability the reaction is the same at both temperatures. Assuming that the same reaction takes place at 100°, 130° and 150° C, the results obtained lead to a very important conclusion with respect to the temperature coefficient of the rate of decomposition.

The following is a general formula:

$$-\frac{dc}{dt} = k_1 f(c) \text{ or } k_1 t = - \int \frac{dc}{f(c)} + C.$$



If therefore we determine the times in which the same quantity decomposes at different temperatures we find:

$$\frac{t_1}{t_2} = \frac{k_2}{k_1} = \text{the temperature coefficient.}$$

We find:

TABLE IV

DETERMINING THE TEMPERATURE COEFFICIENT WITH DRY HEATING, SPECIMEN A<sub>2</sub>

Temperature	Time lapse until 0.29% of Cl is split off	Coefficient per 10° C
150° C .....	1.25 hrs.	2.4
130° C .....	7.3 hrs.	2.4
100° C .....	1000 hrs. (by extrapolation)	5.2

From 150° to 130° C we accordingly find a temperature coefficient of normal magnitude, but from 130° to 100° C an abnormally great one. It is therefore very probable that the rate of reaction declines very quickly below 100° C. In other words there will be hardly any thermal decomposition of chlorinated rubber at temperatures below 100° C.

In summary, we see that the study of dry heating of a specimen of chlorinated rubber has yielded the following results:

(1) That about 0.2% chlorine is split off in 700 hours at 100° C; about 0.4% in 14 hours at 130° C; about 0.3% in 1 hour at 150° C.

(2) That in this specimen the total amount of chlorine which can be split off by dry heating at 130° C was about 0.6%.

(3) That the decomposing reaction shows an abnormally high temperature coefficient at about 100° C.

#### (b) *Heating in Water.*

The Merz Method<sup>7</sup>, whereby chlorinated rubber is heated in water, is much more easily applied than the dry heating method. It must, however, be pointed out that the various kinds of chlorinated rubber powder are not wetted by the water, and float on it, although their specific gravity is 1.7. They were consequently wetted with alcohol beforehand. Glass beakers, each with a capacity of 300 cc., containing about 200 cc. of water and 5 grams of chlorinated rubber were placed in an electrically heated steam bath, covered with a glass disc, and heated for 500 hours (temperature in beaker 96° to 97° C). Each day the contents were neutralized with 0.1 *N* alkali, methyl red being used as indicator, and the evaporated water replaced. At the end of the experiment the total amount of chloride was again determined. It was found that chlorine splits off more quickly when heating wet chlorinated rubber than when heating the same dry (see Figure 1).

The results of the experiments recorded in Figure 2 show that it is not the presence of a certain quantity of CCl<sub>4</sub> in the specimen which is the cause of this difference. To prove this, a comparison was made between an original specimen heated in water with a specimen of chlorinated rubber which had already been heated dry for 722 hours at 100° C. The latter specimen had lost all or the greater part of its CCl<sub>4</sub> content during the dry heating, yet when heated in water almost exactly the same amount of hydrogen chloride was split off from this specimen as from the original specimen.

A careful study of the 3 curves in Figure 2 leads to the conclusion that the decomposition of chlorinated rubber due to dry heating and the splitting off of hydrogen chloride due to prolonged heating in water are not to be regarded as the same reaction.

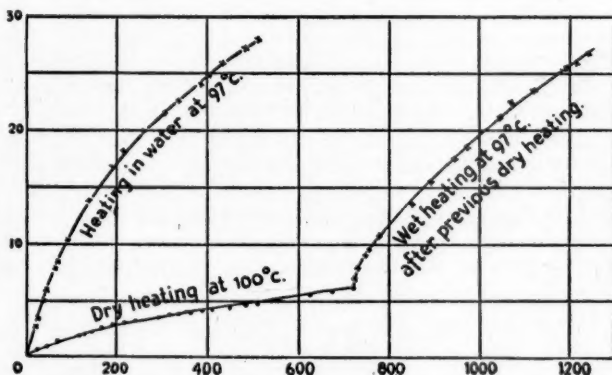


FIG. 2.—The splitting off of hydrogen chloride acid by wet and dry heating of chlorinated rubber (Specimen A<sub>2</sub>).

From the three curves the following maximum quantities of chlorine which can be split off can be calculated (Table V).

The quantity of chlorine which can be split off by heating in water was accordingly not decreased through the dry heating. From the figures in the last

TABLE V

CALCULATED MAXIMUM AMOUNT OF CHLORINE WHICH CAN BE SPLIT OFF WITH DRY AND WET HEATING AT 100° C, SPECIMEN A<sub>2</sub>

Calculated on the values of Z and (dc/dt) after hours .....	100 700	200 700	300 700	400 700	500 700	600 700	Total amount of chlorine split off HCl split off
Dry heating .....	0.35%	0.51%	0.60%	0.67%	0.86%	0.76%	1.14
	100 400	200 400	300 400	500 400	—	—	—
Wet heating .....	1.21%	1.34%	1.37%	1.52%	—	—	1.15
Wet heating subsequent to dry heating (722 hrs.)..	1.57%	1.53%	1.48%	1.48%	—	—	1.34

column, the conclusion may be drawn that not only hydrogen chloride, but also neutral chlorides (NH<sub>4</sub>Cl ?) are split off.

Summarizing, we find that the quantitative determination of chlorine split off during the heating process makes it possible to determine the portion of the maximum quantity of chlorine which can be split off. This quantity is, however, twice as great in the case of wet heating as in the case of dry heating. With heating in water therefore a heterogeneous reaction (hydrolysis ?) is to be contended with.

The method of wet heating proved to be most serviceable for comparing the stability of several specimens of chlorinated rubber, and was consequently applied for this purpose during the investigation.

#### DETERMINING THE QUANTITY OF CHLORINE IN CHLORINATED RUBBER

We required an exact method for the determination of the chlorine content. First of all we applied the customary sodium peroxide method. This method, whereby a mixture of 0.2 gram of chlorinated rubber with 0.2 gram of salicylic acid and 13 grams of  $\text{Na}_2\text{O}_2$  is ignited by means of a red-hot iron wire, then boiled with water and sulfite, after which the dissolved chlorine is gravimetrically determined as  $\text{AgCl}$ , has been improved by the Laboratory of the N.V. Pieter Schoen & Son, of Zaandam (Holland)\*. By adding 0.2 gram of sulfur to the combustion mixture, the process of combustion is considerably quieter and more regular. In spite of this improvement the results still show slight deviations, as will be seen from Table VI.

TABLE VI  
DETERMINING THE AMOUNT OF CHLORINE BY THE SODIUM PEROXIDE METHOD

Specimen	Found (%)	Control (blank)* (%)	% corrected	Determined according to ter Meulen	
				Found %	Average %
A <sub>2</sub>	66.9	0.8	66.1	67.9	68.0
	68.1	0.9	67.2	68.1	—
B <sub>2</sub>	65.5	0.8	64.7	65.4	65.45
	64.9	0.1	64.8	65.5	—
C	64.6	0.9	63.7	66.6	66.65
	66.1	0.3	65.8	66.7	—
D	63.8	0.8	63.0	63.5	63.55
	63.9	0.8	63.1	63.6	—

As the importance of the chlorine content in chlorinated rubber is at present generally recognized, and as it is therefore desirable to determine this chlorine content very exactly, the peroxide method was dispensed with, and the Ter Meulen and Heslinga method of hydrogenation<sup>9</sup> adopted (this method had already been applied by Fol and Bijl). After a few initial difficulties had been overcome, this method yielded excellent results and, with only insignificant deviations from the prescriptions given by Ter Meulen and Heslinga, was executed as follows for routine analysis of chlorinated rubber:

About 130 milligrams of the frequently very voluminous material are weighed out in a large nickel boat. The boat is placed in a quartz tube (80 cm. long; 1 cm. inside diameter) previously thoroughly heated and again cooled, but not yet filled with hydrogen. To prevent the highly electrically charged and flocculous material from adhering to the wall of the quartz tube when the boat is being slid in, the wall of the tube is first breathed on. The boat is slid into the tube to a distance of 12 cm. from the hydrogen inlet. The nickel roll in the incandescent zone to the rear of the boat is left off, no tar being formed in hydrogenating the chlorinated rubber. After the boat is slid in, a continuous stream of hydrogen charged with ammonia is conducted through the tube. A second boat<sup>10</sup> is filled with chlorine-free barium carbonate and slid into the other

\* Private Communication by J. Rinse.

end of the quartz tube. As soon as all the oxygen is removed from the tube, the three Bunsen burners (see Figure 3) are lighted and the mechanical burner transporter is set in motion. The starting point of the moving flame is about 2 cm. to the rear of the boat; the motion of the flame is very slow; the entire boat is glowd out in 75 to 90 minutes. The current of hydrogen, which is conducted through a flask filled with ammonia, should pass at the rate of two to three bubbles per second; for the rest, the apparatus needs no attention during the process of hydrogenation. When the process is completed, a few particles of carbon remain in the boat. Small quantities of  $\text{NH}_4\text{Cl}$  which were sublimated in the opposite direction to the hydrogen current were removed by resublimation. We then cooled the tube and its contents, emptied the contents of the  $\text{BaCO}_3$  boat into a titration beaker, washed the tube, rinsed it with acetic acid, boiled the liquid for one minute, added now some nitric acid and exactly 25 cc. of 0.1 N  $\text{AgNO}_3$  with the aid of a pipette, and boiled for 20

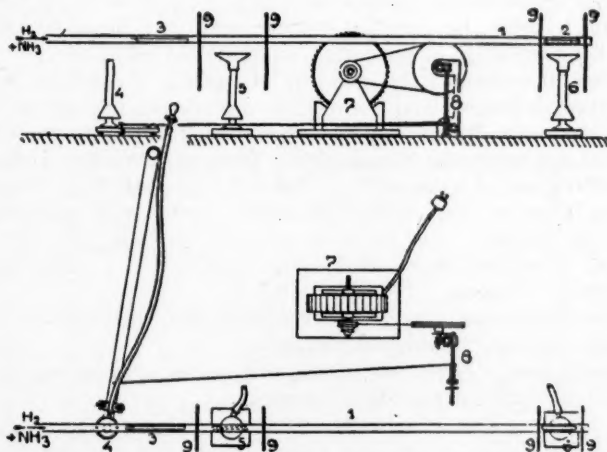


Fig. 3.—Apparatus for the exact determination of the Cl content in chlorinated rubber by hydrogenation.

1. Quartz tube; diameter 1 cm., length 80 cm.
2. Nickel boat with  $\text{BaCO}_3$ .
3. Nickel boat with some 180 mg. chlorinated rubber.
4. Bunsen burner, movable by a little "Saja" synchronous motor (100 rev./min.) [7] and by a double worm gear (1:400).
- 5 and 6. Bunsen burners with slotted mouth.
9. Asbestos screens after ter Meulen.

minutes; after the mixture was completely cooled down, we titrated it with 0.05 N  $\text{NH}_4\text{CNS}$  from a microburette, using sulfate-free ferri solution as an indicator. The duplo determinations, given in Table VI, serve as a measure for the exactitude of the method.

#### REPRECIPITATION AND FRACTIONING OF CHLORINATED RUBBER

As we now had a serviceable stability test and an exact method of determining the chlorine content, the 8 specimens of chlorinated rubber at our disposal were subjected to both tests. On one occasion, however, we also purified specimen  $A_2$ , and by fractional reprecipitation split it up into several fractions in the hope that in this way we should obtain the absolutely stable part of the chlorinated rubber free of all other substances. Furthermore, we hoped to im-

prove the color and clarity of the solutions by purifying the chlorinated rubber. We shall first of all give the results of these experiments.

The chlorinated rubber was purified:

- (a) By removal of insoluble parts.
- (b) By dissolving it in benzene and precipitating it with an excess of alcohol.
- (c) By dissolving it in benzene or carbon tetrachloride and partially precipitating (fractionizing) it with alcohol.

(a) *Removing insoluble components.*

It frequently happens that solutions of commercial chlorinated rubber are not entirely colorless and are sometimes turbid. This turbidity forms a sediment when the solution is allowed to stand for a long time. The turbidity is of a colloidal nature and is difficult to remove; by filtering with filter paper the turbidity could not be retained at all; with a Gooch tile we obtained 0.97% sediment from a solution of 2 grams of specimen A<sub>2</sub> in 40 cc. of benzene; this sediment can, however, be partially washed away with benzene. One also obtains a smaller percentage of precipitate from diluted solutions.

With a view to examining the sediment, 100 grams of specimen A<sub>2</sub> were dissolved in 750 cc. of benzene and the solution was allowed to stand in a separator funnel for eight days. By diluting the sediment with benzene and centrifuging, 0.123 gram of dry substance was obtained; from the partially clarified solution a further 0.056 gram of sediment was obtained by centrifuging. Even then the solution was, however, not entirely clear. By fusing with soda, the chlorine content of the sediment was found to be 17.5 per cent. By the Kjeldahl method, 8.2% of nitrogen was found in the substance, i. e., 10% calculated on the chlorine-free substance.

From these figures we are able to conclude that the sediment came from the "insoluble" part of the original rubber<sup>11</sup>.

This insoluble part is either partially chlorinated or is to be regarded as being intimately mixed with the chlorinated rubber.

(b) *Dissolving chlorinated rubber in benzene and precipitating it with alcohol.*

When a solution of chlorinated rubber in benzene is poured into 95% alcohol, we obtain a soft mass from which one can only partly remove the benzene by kneading with alcohol.

When, however, we slowly add a solution of about 4% of chlorinated rubber in benzene to about 10 times as much 95% alcohol, while the latter is being vigorously stirred, the chlorinated rubber assumes an extremely fine fibrous form. In this form the chlorinated rubber can be dried in a few hours at 80° C down to absolutely constant weight. If a less concentrated solution is used, we obtain a kind of sol when we pour it into alcohol, and when this sol is heated or allowed to stand it soon flocculates. When this precipitate is filtered, we obtain an extremely fine powder.

We first of all determined what portion of the chlorinated rubber (specimen A<sub>2</sub>) is lost when it is precipitated from solution. To this end the filtrate was put in a porcelain dish, evaporated and weighed.

In ten different instances we regained 87.1 to 88.7%, with an average of 88.2% of chlorinated rubber, while 1.8 to 2.5%, with an average of 2.1% remained after the filtrate had been evaporated. Specimen A<sub>2</sub> therefore contained about 9.7% of volatile substances.



The fraction of 2.1% obtained by evaporating the alcohol consisted of a rather viscid brown mass<sup>12</sup>, which was not examined. By determining the amount of chlorine, we endeavored to ascertain how often reprecipitation was necessary to remove all admixtures.

There is, therefore, no doubt that much foreign material is removed from the chlorinated rubber by three reprecipitations. In further analyses we accordingly carried out three reprecipitations beforehand in the manner described.

The data above make it appear that the volatile part of the chlorinated rubber (specimen A<sub>2</sub>) consists exclusively of carbon tetrachloride, for, as already stated, 10% of the specimen is volatile. Carbon tetrachloride contains 92.2% of chlorine, the pure chlorinated rubber 65.25%, the mixture (the original specimen A<sub>2</sub>) therefore 67.9%, which is the figure really found.

The chlorinated rubber obtained by reprecipitation splits off a considerably smaller quantity of chlorine when heated with water. We shall revert to this in the next paragraph.

TABLE VII

THE EFFECT OF REPEATED REPRECIPITATION ON THE CHLORINE CONTENT OF CHLORINATED RUBBER (SPECIMEN A<sub>2</sub>)

	Chlorine content (%)	Average (%)
Original .....	67.9—68.1	68.0
After 2 reprecipitations.....	65.3—65.2	65.25
After 4 reprecipitations.....	65.4—65.1	65.25

(c) *Fractional precipitation from the solution.*

When alcohol is added in small quantities to a solution of chlorinated rubber in benzene or carbon tetrachloride, the liquid soon divides into two layers<sup>13</sup>, the upper layer containing benzene, alcohol and some chlorinated rubber; the lower layer principally chlorinated rubber and benzene. Figure 4 is a representative solubility diagram. Actually, however, the situation becomes much more complicated, owing to the fact that the chlorinated rubber in the upper layer has other characteristics than those of the lower one.

When specimen A<sub>2</sub> was fractionated, the chlorinated rubber in the upper layer was less viscous, had a greater chlorine content, was more stable and less colored; a film of this chlorinated rubber exposed to the effect of sunlight for some months did not become nearly so yellow as the original specimen<sup>14</sup>. This fraction of the chlorinated rubber is, moreover, absolutely clear, and shows no signs of turbidity<sup>15</sup>. Furthermore, there are obvious indications that the chlorinated rubber from the upper layer makes films which are surprisingly less brittle than films made from the original chlorinated rubber.

We carried out more fractionating experiments, both with chlorinated rubber in benzene solutions and in carbon tetrachloride solutions; the latter solvent is advantageous, because the layers are formed more distinctly, owing to their greater difference in density. The alcohol is best added as a mixture of alcohol and CCl<sub>4</sub>, since otherwise lumps of a mixture of chlorinated rubber and solvent will form, and these lumps are difficult to break up.

Below we give further particulars of one of the fractionations carried out with carbon tetrachloride solution.

We shall revert to the stability and chlorine content figures later. From the amount of chlorine split-off given in Table VIII, it will be seen that the fractions obtained first are really better; the great differences in viscosity are remarkable. The determinations of the chlorine content alone bring one to the conclusion that there is a definite difference between the chlorine content of the remaining material and the chlorine content of the fractions obtained by extraction. This is probably due to various impurities having assembled in the remaining material.

A definite relation between the chlorine content on the one hand and viscosity or stability on the other, as is from time to time asserted in the literature, most certainly does not exist in the case of the fractions of these specimens of chlorinated rubber.

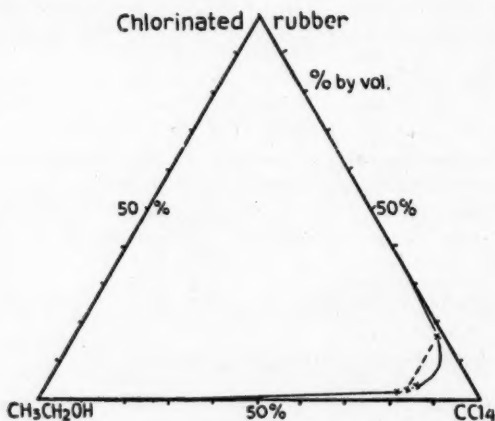


FIG. 4.

We might close this section with the conclusion that it is indeed possible to isolate a high-quality product from common commercial chlorinated rubber by purifying and fractionating.

#### RESULTS OF STABILITY AND CHLORINE CONTENT DETERMINATIONS

The commercial specimens at our disposal and some of the prepared fractions were kept in hot water ( $96^{\circ}\text{C}$ ) for 500 hours after one reprecipitation, and the curve indicating the amount of chlorine split off was plotted. The total amount of chlorine split off in 500 hours was determined directly; the figure for the maximum amount of chlorine which can be split off was calculated from the curve indicating the amount of hydrogen chloride split off and then multiplied by the quotient of the total amount of chlorine split off and acid split off. It will be seen from Table IX, where the values of  $C_0$  calculated from several pairs of points are given side by side, that the calculation of the quantities of chlorine which can be split off is, in the case of these specimens of chlorinated rubber, which have been purified by reprecipitation, really justified; in other words, that the decomposition reaction is really monomolecular (or pseudo-monomolecular).

One cannot expect better agreement, in view of the fact that the graphical determinations of  $dc/dt$  from the curves are far from exact. The chlorine

TABLE VIII  
FRACTIONAL PRECIPITATION OF SPECIMEN A<sub>2</sub> FROM A SOLUTION IN CARBON TETRACHLORIDE

	Fraction					Original material 100%
	I	II	III	IV	V	
Starting mixture: 250 g. A <sub>2</sub> dissolved in 1500 cc. of CCl <sub>4</sub>						
Added (260 cc. alcohol + 260 cc. CCl <sub>4</sub> ).....						
Lower layer	14.9%	—	—	—	—	—
+ (150 cc. alcohol + 400 cc. CCl <sub>4</sub> ).....	—	6.1%	—	—	—	—
+ (70 cc. alcohol + 500 cc. CCl <sub>4</sub> ).....	—	—	10.3%	—	—	—
+ (70 cc. alcohol + 400 cc. CCl <sub>4</sub> ).....	—	—	—	11.8%	—	—
+ (70 cc. alcohol + 400 cc. CCl <sub>4</sub> ).....	—	—	—	—	8.6%	—
Rest .....	—	—	—	—	—	47%
REMARKS						
Color of the solution.....	Yellow	Yellowish	A little yellowish	Nearly colorless	Nearly colorless	Brownish
Turbidity of the solution.....	Clear	Clear	Clear	Clear	Clear	Turbid
Viscosity (Cochius, tube 50 cm., diameter 7 mm., time in sec.).....	11	19.5	65.75%	21.5	65.95%	59
Chlorine content (after 3 reprecipitations)....	65.95%	0.53	0.62	0.26	0.98	65.25%
% Cl split off at 100° C after 500 hours.....	0.40	0.41	0.41	0.41	0.41	0.60
Maximum % Cl which can be split off.....	0.41	0.41	0.41	0.41	0.41	1.01

content figures were determined in duplicate, and are given together with the other figures in Table X.

It may be observed that in the case of both the chlorinated rubber specimens A and B, with the exception of A<sub>1</sub>, the specimen with a higher viscosity had a lower chlorine content than the low-viscosity specimen. As, however, no confirmation of this relation between viscosity and chlorine content was previously found in the fractions of specimen A<sub>2</sub>, we will not assert that chlorinated rubber of high viscosity has a smaller content of chlorine. It is very well possible that the difference in the chlorine content of the specimens A<sub>1</sub>-A<sub>3</sub> and B<sub>1</sub>-B<sub>3</sub> is due to peculiarities in the chlorination of rubber solutions of different viscosities<sup>16</sup> during the manufacturing process.

TABLE IX

THE VALUES OF C<sub>0</sub> CALCULATED FROM SEVERAL PAIRS OF POINTS FOR THE WET HEATING OF VARIOUS SPECIMENS OF CHLORINATED RUBBER

Specimen	Calculated from the values of Z and (dc/dt) after h		
	200/400	300/400	500/400
A <sub>1</sub> .....	0.64	0.73	0.56
A <sub>2</sub> not reprecipitated.....	1.34	1.37	1.52
A <sub>2</sub> Specimen '32 reprecipitated....	0.71	0.81	0.74
A <sub>2</sub> Specimen '33 reprecipitated....	0.67	0.71	0.74
<hr/>			
	100/200	300/200	400/200
A <sub>2</sub> Fraction I reprecipitated.....	0.21	0.19	0.19
<hr/>			
	200/400	300/400	500/400
A <sub>2</sub> Fraction III reprecipitated.....	0.60	0.60	0.66
A <sub>2</sub> Fraction V reprecipitated.....	0.76	0.75	0.75
B <sub>2</sub> .....	0.55	0.64	0.68
C .....	3.21	2.70	2.47
D .....	0.55	0.66	0.55

## SUMMARY

(1) In ultraviolet rays decomposition occurs in the upper surface of a layer of chlorinated rubber.

(2) The amount of chlorine split off from a common commercial specimen of chlorinated rubber when heated dry for 30 days at 100° C was about 0.25 per cent. For the greater part, the chlorine was free of hydrogen chloride.

(3) The rate of decomposition when dry heating was applied at 100°, 130° and 150° C leads to the conclusion that the speed of reaction diminishes rapidly at degrees below 100° C until there is soon no reaction at all.

(4) The amount of chlorine split off when chlorinated rubber was heated in water at 100° C was about five times as large as when dry heating was applied.

(5) From the curves indicating the amount of chlorine split off during "wet" and "dry" heating at 100° C, it is possible to calculate quantities which may be regarded as the maximum amounts of chlorine which can be split off from the respective specimens. These amounts are twice as large when the chlorinated rubber is heated wet as when dry heating is applied; with a given normal specimen about 1.5 per cent was obtained in wet heating. Only in one of eight specimens was a greater quantity found, viz., 3 per cent.

(6) In a certain specimen 10 per cent of carbon tetrachloride was found. The splitting off of chlorine is not caused by decomposition of this substance.

TABLE X  
RESULTS OF STABILITY AND CHLORINE CONTENT DETERMINATIONS

Specimen	Chlorine content according to ter Meulen		Quotient total amount of Cl split off at 100° C after 500 hours Total amount of acid split off	% Cl split off at 100° C after 500 hours	Total amount of Cl to be split off (in %)
	Found	Average			
A <sub>1</sub> reprecipitated*	65.05—69.0	65.0	1.38	0.56	0.88
A <sub>2</sub> not reprecipitated	67.9—68.1 †	68.0	1.20	1.21	1.69
A <sub>3</sub> (reprecipitated) 1° specimen	65.2—65.3		1.37	0.60	1.03
A <sub>4</sub> (reprecipitated) 2° specimen	65.15—65.3	65.25	1.39		
			2.13	0.61	0.99
A <sub>5</sub> Fraction I (Table VIII) (reprecipitated)	65.9—66.0	65.95	—	0.40	0.41
A <sub>6</sub> Fraction II (Table VIII) (reprecipitated)	65.7—65.8	65.75	—	—	—
A <sub>7</sub> Fraction III (Table VIII) (reprecipitated)	65.8—65.7	65.75	—	0.53	0.62
A <sub>8</sub> Fraction IV (Table VIII) (reprecipitated)	65.8—65.8	65.8	(No acid split off; only chlorine)	—	—
A <sub>9</sub> Fraction V (Table VIII) (reprecipitated)	65.9—66.0	65.95	1.31	0.62	0.98
A <sub>10</sub> Rest (Table VIII) (reprecipitated)	64.7—64.5—64.6 †	64.6	—	—	—
A <sub>11</sub> (reprecipitated)	64.3—64.4	64.35	—	—	—
B <sub>1</sub> (reprecipitated)	67.4—67.4	67.4	—	—	—
B <sub>2</sub> (reprecipitated)	65.4—65.5	65.45	1.43	0.72	0.89
B <sub>3</sub> (reprecipitated)	64.0—64.0	64.0	—	—	—
C (reprecipitated)	66.6—66.7	66.65	1.11	1.34	3.10
D	63.6—63.5	63.55	1.72	0.98	0.98

\* Three reprecipitations for analysis, one reprecipitation for stability test.

† Specimen not entirely homogeneous.



(7) By reprecipitation the quantity of chlorine capable of being split off was reduced from 1.5 to about 1 per cent.

(8) The sediment which usually forms when solutions of chlorinated rubber are allowed to stand consists of the insoluble parts of the original rubber.

(9) Fractions with different characteristics are obtained by fractional precipitation of chlorinated rubber solutions.

(10) The viscosity of the fractions increases when the solubility in a mixture of benzene and alcohol is lower. Films made from the more soluble fractions are definitely less brittle than those made from the original material. The quantity of chlorine split off in the soluble fraction is definitely smaller than that of the original material. Moreover, from these fractions we obtain very light colored and absolutely clear solutions; films made from them do not become so yellow when exposed to sunlight as those made from the original material.

(11) The Ter Meulen method of analysis by hydrogenation is eminently suited for the exact determination of the amount of chlorine in chlorinated rubber.

(12) On the whole no relation was found between chlorine content, viscosity and stability of chlorinated rubber specimens.

## REFERENCES

- <sup>1</sup> Nielsen, "Chlorkautschuk und die übrigen Halogenverbindungen", Leipzig, 1937.
- <sup>2</sup> Fol and Bijl, *India-Rubber J.* **83**, 620 (1932); *Farben-Zeitung* **37**, 1377 (1932); *Chem. Weekblad* **29**, 162, 448 (1932).
- <sup>3</sup> Irradiation was carried out by means of a quartz mercury lamp, using about 140 watts in the discharge tube, at a distance of 6 cm. The copper strips became only slightly warm by the irradiation.
- <sup>4</sup> The copper-strip test is fairly frequently applied for testing the quality of chlorinated rubber. The test is, in fact, very simple and rapid for determining resistance to ultraviolet rays; in this connection one should always use a layer of equal thickness, as was also noted by Rosenthal and Schultz (*Farben-Chemiker* **5**, 53 (1934)). This irradiation test is, however, by no means a general stability test. A copper sublayer is only used because the copper quickly reveals the forming of decomposition gases. There is no direct reaction between copper and chlorinated rubber the rate of which might serve as a criterion by which to determine the stability of chlorinated rubber in general, as the following test will show. An intimate mixture of very fine copper powder and pulverized chlorinated rubber was subjected to the rays of a quartz lamp in a closed quartz flask, the flask being frequently shaken during the process of irradiation. The distance and the lamp were the same as in the case of the copper strips; duration 8.5 hours; the temperature inside the flask was 40-60° C. At the same time an identical quantity of chlorinated rubber without copper was subjected to the rays of the lamp, during which process care was taken that the two flasks were frequently changed about. The HCl which was split off was absorbed in water placed in a test tube in the flask. After the test, the contents of the flask (powder and test tube) were washed 15 times with boiling water. The chloride in the filtrate was determined by the Volhard method. The copper powder had become black under the rays of the lamp; when the powder was treated with diluted nitric acid after being washed it resumed its color. There was, however, no measurable quantity of Cl ions in the acid. The following results were obtained:

	% Cl in chlorinated rubber *		
	Not radiated	Radiated	% Difference
Chlorinated rubber .....	0.011	0.084	0.073
Chlorinated rubber with copper powder (ratio by weight 1:2) .....	0.012	0.086	0.074

\* In the wash-water.

The presence of metallic copper accordingly has no effect on the decomposition of chlorinated rubber in ultraviolet rays.

<sup>5</sup> The water which condensed in the connecting tube between the U-tube and the absorption vessel, especially at the beginning of the heating was carefully conducted to the absorption vessel.

<sup>6</sup> This figure agrees with that arrived at by Rinse (*Chem. Weekblad* **29**, 37 (1932)), 4.8% in 400 hours.

<sup>7</sup> Merz, *Kautschuk* **2**, 80 (1933).

<sup>8</sup> The blank values are fairly high; by using reagents with a low chlorine content it was possible to reduce the blank value to 0.1 or 0.2%; the concordance between the found chlorine contents in one and the same specimen was, however, not favorably influenced by this.

<sup>9</sup> *Recueil Trav. Chim.* **47**, 698 (1928).

<sup>10</sup> The use of a porcelain boat for the calcination of the BaCO<sub>3</sub> was found to be undesirable, because when the calcination temperature is a little too high, or when calcination is prolonged for some length of time, a fairly considerable amount of Cl is adsorbed by the porcelain or its glazing, retained for a time and later again released. When a porcelain boat was used for BaCO<sub>3</sub>, which is indispensable for breaking up NH<sub>4</sub>Cl clouds, we almost invariably found high and changing blank values. It is probable that the difficulties in determining the blank values described by Fol and Bijl (*Chem. Weekblad* **29**, 448 (1932)) are also to be attributed to this.

- <sup>11</sup> Dekker (Communication "Rijksvoorlichtingsdienst t.b.v. den Rubberhandel en de Rubbernijverheid. Delft", 2nd series, 1916, pages 488-551; *Kolloidchem. Beihefte* 62 (1918)) determined the insoluble portion in several specimens of rubber by prolonged heating in petroleum; the amounts found were about 3%. This would accordingly be 1% in chlorinated rubber, which figure agrees with the greatest amount found by the writer. The N-content of the insoluble fraction in rubber (i.e. page 505 = 10.5%) likewise agrees with the N-content of the insoluble fraction in chlorinated rubber.
- <sup>12</sup> It is possible that this mass contains not only impurities, e.g., the "insoluble" parts of the original rubber and perhaps oxydation products, but also the parts of the chlorinated rubber with a very low molecular weight.
- <sup>13</sup> Considered from a colloid chemical point of view, we have here a stable coacervation (Bungenberg de Jong and Kruyt, *Kolloid-Z.*, 50, 39 (1930)).
- <sup>14</sup> This difference was not clear when exposed to ultraviolet light; the absorption of ultraviolet rays is after all a characteristic of the chlorinated rubber molecules themselves (see Nielsen, note 1).
- <sup>15</sup> Midgley, Henne and Renoll (*J. Am. Chem. Soc.* 53, 2733 (1931)) fractionated rubber solutions in a very similar way. They likewise found that all impurities remained (the more soluble part was obtained entirely nitrogen free). The authors also observed that the soluble part of the rubber could no longer be precipitated with acetone; in other words that it manifested other characteristics than the original rubber.
- <sup>16</sup> Cf. Nielsen, note 1, page 31.

# STUDIES OF HARD RUBBER REACTIONS

## VI. LIBERATION OF SO-CALLED FREE SULFUR AND CHANGES IN THE ACETONE EXTRACT OF VULCANIZED RUBBER BY REPEATED EXTRACTION AND HEATING \*

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It was found in previous experiments<sup>1</sup> that a portion of the sulfur in soft and in hard vulcanized rubber exists always in the free or acetone-soluble state. Much has already been studied on this problem concerning the theory of vulcanization<sup>2</sup> but, strictly speaking, no satisfactory conclusions have yet been reached.

In the present investigation, the author conducted the following experiments to ascertain the formation or origin of free sulfur and also of acetone extract in vulcanized rubber during repeated extraction and heating.

### EXPERIMENTAL

Mixings: Rubber 100, zinc oxide 10, stearic acid 1, diphenylguanidine 2, sulfur 5, 25, 100 and 150.

Cures: 60, 180 and 300 minutes at 141° C.

Each vulcanized rubber sample was extracted with acetone for 20 hours, in an atmosphere of nitrogen to avoid oxidation. The residue was then transferred to a U-tube, the air in which was replaced by a current of nitrogen, and was heated for 2 hours in an oil bath maintained as the temperature of vulcanization, i. e., 141° C. The extraction and heating were repeated 10 times.

### SUMMARY OF RESULTS

(1) *Free Sulfur*.—As is evident in Figures 1 to 5, during the whole process of extraction and heating, there are 1 to 3 maxima in the free sulfur curves. The cause of such changes in free sulfur is to be found in the history of the vulcanized product before extraction and heating, i. e., it can be assumed that the depolymerization phenomenon which generally occurs at certain stages of vulcanization reappears, probably as a result of a reduction in the quantity of accelerator, etc., in the original sample by prolonged extraction.

The thermally active sample of 60 minutes' cure showed a maximum comparatively early in the extraction and heating, and the thermally inactive vulcanizates of 180 or 300 minutes' cure showed high and low figures corresponding to the respective states of cure which represented completion of the thermal reaction.

(2) *Acetone Extract*.—In general the course of the changes in acetone extract resembled those in free sulfur, but various differences are evident. In certain cases, the formation of organic acetone-soluble substances showed suddenly high or, on the contrary, low values during extraction and heating. This fact may be ascribed to the formation of some characteristic compounds with reference to the original mixes.

\* Reprinted from *The Journal of the Society of Chemical Industry, Japan*, Vol. 42, Supplemental binding No. 9, pages 319-321B, September 1939.

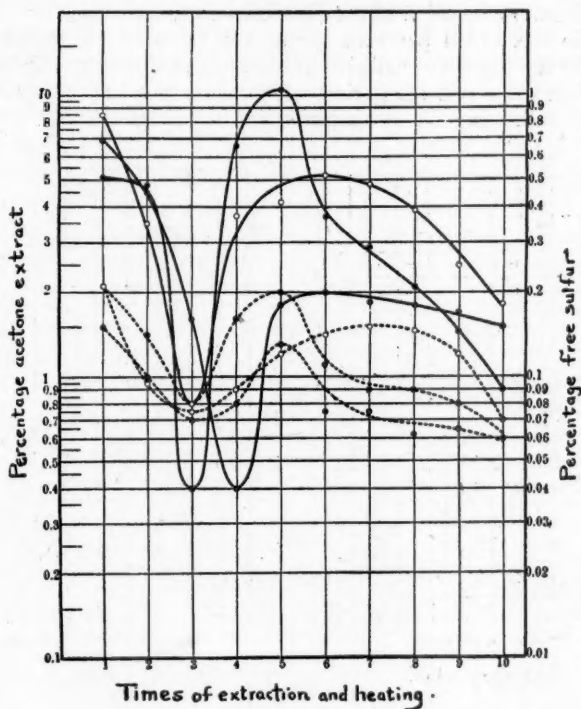


FIG. 1.—5 per cent sulfur.

— Acetone extract.  
 - - - Free sulfur.

○ 60 minutes' cure.  
 ● 180 minutes' cure.  
 ○ 300 minutes' cure.

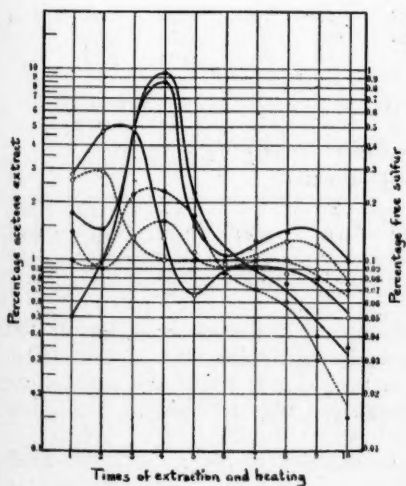


FIG. 2.—25 per cent sulfur.

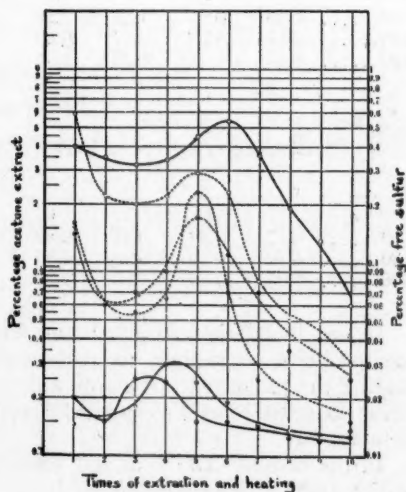


FIG. 3.—50 per cent sulfur.

(3) *Extraction With and Without Heating.*—Parallel with above experiments concerning the mix of 50 per cent sulfur, the results of the single extraction repeated under the ordinary condition of chemical analysis are graphically shown in Figure 6, and those of a comparison of the total free sulfur extracted with or without alternate heating are also represented in Tables 1 and 2.

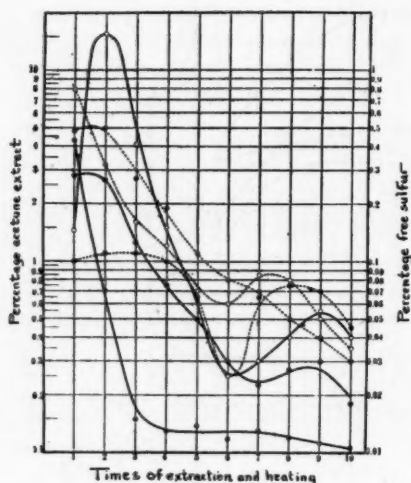


FIG. 4.—100 per cent sulfur.

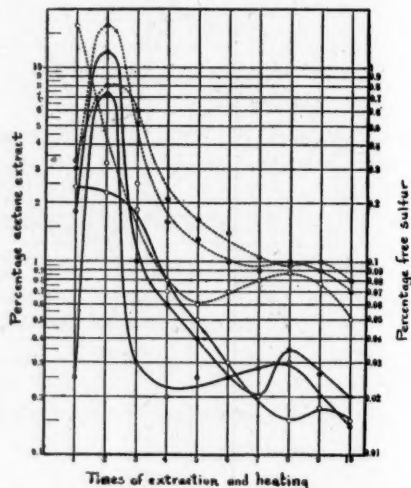


FIG. 5.—150 per cent sulfur.

TABLE I

PERCENTAGE OF TOTAL FREE SULFUR EXTRACTED AFTER HEATING

Minutes of cure	Times of extraction and heating									
	1	2	3	4	5	6	7	8	9	10
60.....	0.59	0.81	1.01	1.23	1.52	1.75	1.83	1.88	1.93	1.96
180.....	0.14	0.20	0.27	0.36	0.53	0.64	0.71	0.75	0.79	0.81
300.....	0.16	0.22	0.28	0.34	0.57	0.64	0.67	0.69	0.71	0.72

TABLE II

PERCENTAGE OF TOTAL FREE SULFUR EXTRACTED WITHOUT HEATING

Minutes of cure	Times of extraction									
	1	2	3	4	5	6	7	8	9	10
60.....	0.17	0.29	0.41	0.52	0.72	0.83	0.89	0.93	0.95	0.98
180.....	0.10	0.20	0.30	0.35	0.44	0.50	0.55	0.59	0.62	0.64
300.....	0.05	0.12	0.19	0.22	0.26	0.31	0.38	0.43	0.45	0.47

It was found that, although the temperature of extraction is as low as the boiling point of acetone, the vulcanizates underwent some kind of heat effect during the prolonged extraction, and the changes in free sulfur and acetone extract followed courses very similar to those which they followed at the higher temperature.

In the case of extraction and heating, the quantity of generated or liberated sulfur from vulcanizates, probably by depolymerization, was evidently greater than that of ordinary low temperature extraction.



Considering the above results, it is noted that the theories maintaining the necessary existence of free sulfur, and the possibility of its complete extraction from vulcanized rubber, might be started from the erroneous ground which ignored the depolymerization phenomenon of vulcanized rubber products, etc., in the course of extraction.

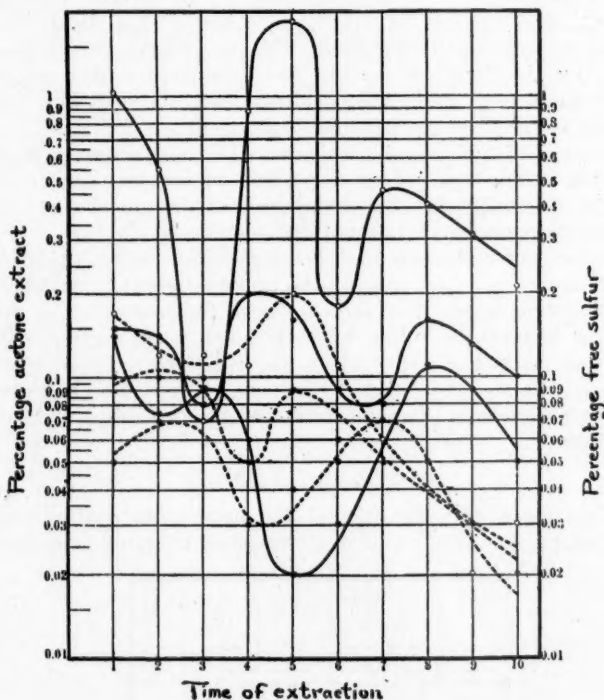


FIG. 6.—50 per cent sulfur.

#### REFERENCES

- <sup>1</sup> Numaziri, J. Soc. Chem. Ind., Japan **39**, 221B (1936); **40**, 111B (1937).
- <sup>2</sup> Höhn, *Gummi-Ztg.* **14**, 17, 33 (1899); Buizov, *Kolloid-Z.* **7**, 160 (1910); Spence and Scott, *Kolloid-Z.* **8**, 304 (1911); Kirchhof, *Kolloid-Z.* **13**, 49 (1913); **14**, 35 (1914); **26**, 168 (1920); Harries, *Ber.* **49**, 1390 (1916), Ostwald, *Kolloid-Ztg.* **6**, 136 (1910); Bary, "Le Caoutchouc", 1936, 207.

### VII. TRUE FREE SULFUR FROM PURE RUBBER-SULFUR COMPOUND, AND CHANGES IN ACETONE EXTRACT DURING REPEATED EXTRACTION AND HEATING \*

SEIITI NUMAZIRI

It was reported in Part VI that a portion of the sulfur may always be extracted as free sulfur, probably due to depolymerization, etc., from the vulcanized product, by extraction and heating.

\* Reprinted from *The Journal of the Society of Chemical Industry, Japan*, Vol. 42, Supplemental binding No. 9, pages 369-370B, November 1939.

Further experiments were undertaken with the pure rubber-sulfur compound to ascertain the liberation of true free sulfur, as well as the formation of acetone-extractable organic substances by repeated extraction and heating.

#### EXPERIMENTAL

(a) *Method for purifying latex.*—Deproteinized, deresinated pure rubber was prepared from concentrated 75% latex. The first cream, treated with alkali digestion, was separated and recream. This was dialyzed through cellophane and coagulated with dilute acetic acid. The coagulated rubber was washed on laboratory stainless steel washing rolls, dried and extracted with acetone.

The product obtained contained 0.04% nitrogen.

(b) *Preparation of vulcanized specimens.*—The experimental procedure for the mastication, mixing and curing of purified rubber was similar to that described in Part I<sup>1</sup>, except that the composition of the mixture was rubber 100, sulfur 50, and the cures were 120 and 300 minutes at 141° C.

(c) *Treatment for extraction and heating.*—This treatment also was conducted in the same way as described in the previous report (part VI).

(d) *Determination of true free sulfur.*—As to the free sulfur in the ordinary sense, the true elementary sulfur was separated from organic sulfide sulfur by the analytical method of Kelly<sup>2</sup> which was somewhat modified by the author.

(e) *Acetone extract.*—The corrected acetone extract was calculated as the difference between the total acetone extract and the free sulfur and sulfide sulfur soluble in acetone.

#### SUMMARY OF RESULTS

1. *True Free Sulfur.*—In the case of the pure rubber-sulfur compound, as shown in the graph, the quantity of true free sulfur liberated from the thermally

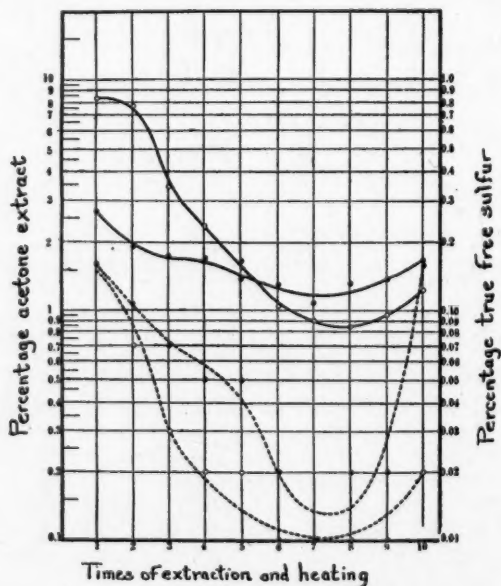


FIG. 1.—Pure rubber-sulfur (50% S).

— Acetone extract.  
 - - - True free sulfur.  
 ○ 120 min. cure.  
 ● 300 min. cure.

active hard rubber product by 120 minutes' cure was generally a little greater than that from the thermally nonactive sample with 300 minutes' cure. During the whole course of the extraction and heating, there occurs a lowest point in the true free sulfur curve, which increases again. In view of this fact, liberation of free sulfur can not be attributed to the insufficiency of the acetone extraction but is probably attributable to depolymerization of the vulcanizate or the like.

2. *Acetone Extract*.—Although purified rubber was used, the corrected acetone extract due to the formation of resinous substances from the depolymerized or aged hard rubber product showed relatively high values at the beginning of extraction and heating.

To some extent, the change in acetone followed a course similar to that of the true free sulfur.

#### REFERENCES

- <sup>1</sup> *J. Soc. Chem. Ind., Japan* **39**, 76B (1936).  
<sup>2</sup> Kelly, *J. Ind. Eng. Chem.* **12**, 875 (1920).

# APPLICATIONS OF THE MANOMETRIC METHOD FOR MEASURING THE OXIDIZABILITY OF RUBBER

## OXIDIZABILITY AND AGING IN THE GEER OVEN \*

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### INTRODUCTION

Since oxygen is the chief cause of the deterioration of rubber, it is only natural to consider the use of the manometric method, already used to measure oxidizability, for detecting signs of aging in rubber. Like all other tests devised for this same purpose, the manometric test is naturally subject to certain reservations which have already been described by one of the present authors.<sup>1</sup>

In the present paper, it is proposed to compare the manometric test with another accelerated aging test which has been generally accepted, the Geer oven test. Two questions will be considered.

(1) Is there any correlation between the oxidizability of a given rubber mixture and its behavior in the Geer oven?

(2) Do the manometric test and Geer oven test classify a series of different rubber mixtures in the same order?

In the present treatment of the subject, the relations between the measurement of oxidizability and the prediction of natural aging are not considered.

### CORRELATION BETWEEN OXIDIZABILITY AND THE GEER OVEN TEST

It is not possible to compare directly readings in the manometric test<sup>2</sup> with mechanical tests of samples aged in the Geer oven. Nevertheless, since a manometric measurement is nothing more than a measure of the oxygen absorbed, a basis of comparison is to be had by measuring the losses in tensile strength of Schopper rings which have already absorbed known proportions of oxygen.

However, the dimensions of the manometric apparatus are not great enough to allow the oxidation of samples as large as Schopper rings. Accordingly recourse was had to the old type of apparatus constructed completely of glass, which will be described briefly later.

### OXIDATION OF SAMPLES

The mixture chosen for the experiments had the following composition:

Smoked sheet .....	100
Sulfur .....	2.5
Tetramethylthiuram disulfide .....	0.20
Benzothiazyl disulfide .....	0.25
Stearic acid .....	1
Zinc oxide .....	5
Clay (kaolin) .....	40

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from an abridged reprint of an article in *Caoutchouc et Plastiques*, Vol. 2, p. 87.

A weight of approximately 1.49 grams of this mixture is taken to obtain 1 gram of actual rubber.

The mixture was vulcanized in a hydraulic platen press for 10 minutes at 143° C. The addition of an antioxygen was purposely omitted so that the time of measurements would not be unduly prolonged.

Sixteen rings, ready for testing on a Schopper dynamometer, were oxidized to different degrees in the following way. Two rings were placed in a crystal-glass flask of 100 cc. capacity, which was joined to the bent end of a vertical tube of small diameter. Eight such flasks, each containing two test-rings, and a ninth flask, serving as a blank, composed a unit of nine manometers joined to a single horizontal tube. The entire system was evacuated and filled with oxygen. Mercury was then introduced through the horizontal tube, and it ascended to a definite height in each vertical tube and thus shut off each flask. The flasks were kept immersed in an oil bath maintained at 80° C, and in each case the ascent of mercury, which was proportional to the oxygen absorbed, was measured.

By knowing the volume of the flask, the inside diameter and length of the manometric tube, and the weight and volume of the rings, it is easy to calcu-

TABLE I

Flask No.	Total weight of 2 rings before oxidation	Increase in weight after oxidation	Degree of oxidation (percentage)	
			Based on ascent of mercury	Based on increase in weight
1.....	4.2841	0.0074	0.2	0.25
2.....	4.3542	0.0109	0.4	0.37
3.....	4.3183	0.0174	0.6	0.60
4.....	4.2989	0.0231	0.8	0.80
5.....	4.3364	0.0292	1.0	1.00
6.....	4.3408	0.0344	1.2	1.18
7.....	4.3396	0.0400	1.5	1.37
8.....	4.3195	0.0368	2.0	1.27

late the ascent of the mercury corresponding to any degree of oxidation. It may be assumed, as a first approximation, that the temperature of the gas was 80° C inside of the flask and 20° C in the manometric tube. When the mercury reached the desired point of ascent, the flask was shut off.

The test-rings were first brought to constant weight over phosphorus pentoxide in a desiccator and, after their final weighings, were placed in the flasks. After having been oxidized, they were again weighed, and the degree of oxidation was expressed in terms of the percentage of oxygen absorbed by weight, based on the actual rubber.

As is evident in Table I, the results obtained show that the gravimetric measurements agreed with the volumetric measurements only to a degree of oxidation corresponding to approximately 1 per cent. Beyond this point, the weights were no longer of any significance for water and undoubtedly other oxidation products as well were liberated. The volumetric method of measurement is subject to much less error, for the water condenses on the cold wall and only its vapor pressure at room temperature influences the result.

Eight flasks of a second series, again with 2 test-rings in each flask, were sealed in a vacuum (by a mercury pump) and held in the oil bath at 80° C. One of the flasks was removed each time that a flask containing the oxidized rings was removed, so that the rings in a vacuum served as control test-specimens which had not been oxidized but had been subjected to the heating at 80° C.



Finally, several identical rings were kept in a vacuum at room temperature and in darkness for the duration of the experiments. Since these rings were neither heated nor oxidized, they represented what might be called the original sample.

By measuring the mechanical properties of the oxidized samples, or the samples heated in a vacuum, and of the original control samples, it was possible to distinguish between the effect of oxidation and the effect of heating. The results are summarized in Table II, in which the losses in tensile strength and in breaking elongation are given as functions of the degree of oxidation.

The data show that the effects of heat alone were relatively small, and that the deterioration was caused, for the most part, by oxidation<sup>3</sup>.

TABLE II

Degree of oxidation (percentage)	Loss in tensile strength (percentage)		Loss in elongation of rupture (percentage)	
	Based on original sample	Based on sample heated in a vacuum	Based on original sample	Based on sample heated in a vacuum
0.2.....	17.7	16.6	7.4	10.9
0.4.....	27.8	26.0	9.4	11.3
0.6.....	39.2	29.2	10.0	13.2
0.8.....	62.0	56.4	27.0	28.9
1.0.....	75.0	69.5	45.5	45.6
1.2.....	84.6	83.0	68.6	70.2
1.5.....	90.0	88.0	90.5	91.0
2.0.....	93.3	92.0	98.3	98.0

## AGING IN THE GEER OVEN

A series of rings of the same composition were placed in a Geer oven, with circulating air, at a constant temperature of 70° C. The aging was continued for six weeks, at the end of which time the rings had lost nearly all of their mechanical properties, as was also true of some of the rings in the oxidation test described above.

The results of the dynamometric measurements are summarized in Table III, in which the relative losses in tensile strength and in elongation at rupture, based on these two properties of the original unaged rings, are recorded.

TABLE III

Time in Geer oven	Loss in tensile strength (percentage)	Loss in elongation at rupture (percentage)
3 days .....	12	0.8
5 days .....	18	4.0
1 week .....	21.2	6.7
11 days .....	34.2	9.0
2 weeks .....	48	12.3
3 weeks .....	82.5	37.6
4 weeks .....	88.6	59.0
5 weeks .....	90.4	89.4
6 weeks .....	92.5	98.5

## COMPARISON OF THE TWO SERIES OF MEASUREMENTS

If a graph is constructed, as in Figure 1, of the losses in tensile strength as a function of the percentage of oxygen absorbed (see Table II), if a second scale is then made on the abscissa to represent the time in the Geer oven, and

if this latter scale is properly chosen, it will be found that the second curve of the loss of tensile strength (from Table III) is practically identical to the first curve.

It follows from this comparison that treatment in the Geer oven brings about changes parallel to those which are caused by oxidation in the manometric apparatus. Hence the same results are obtained whether one measures the cause or the effect, *i. e.*, whether the dynamometric tests are made or whether the degree of oxidation is measured. But in the latter case, it is not even necessary to determine the percentages of oxygen absorbed: it is much simpler to measure a property which is proportional to it, *viz.*, the rate of oxidation or oxidizability.

Obviously it is not necessary to use samples in the form of tensile test-specimens to measure this rate, and it is sufficient to place in the manometric apparatus pieces of stock of any shape whatever cut into small, uniform pieces. Preliminary tests have shown<sup>4</sup> that an increase in temperature makes possible a great increase in the rapidity of the measurements, and recently published work<sup>5</sup>, some results of which are shown in Table IV for the mixture studied in the present work, has proved that the rate of oxidation is approximately 50 times as great at 120° C as it is at 80° C.

TABLE IV

Temperature of test (° C)	Mean hourly ascent of mercury in manometric tube (mm.)
70.....	3
80.....	8
90.....	22
100.....	67
120.....	408

It becomes possible, then, by carrying out the oxidizability test at 80° C, to obtain indications of deterioration in periods of time of the order of one-quarter of an hour, whereas in the case of the majority of industrial rubber mixtures, the Geer oven test does not begin to give any indications of deterioration for about ten days. There is available therefore a rapid control method which satisfies the exacting requirements of present-day industrial technology, and with which it is possible to determine almost at once whether a manufactured article conforms to its previously established standard quality. Incidentally the slowness of the Geer oven test has recently led the R. T. Vanderbilt Company Laboratory<sup>6</sup> to attempt to modernize the test by increasing the temperature.

## COMMENTS

According to Table II and to the curve in Figure 1, the loss of 50 per cent of the tensile strength by the particular samples which were tested corresponds to an absorption of oxygen of approximately 0.7 per cent (based on the rubber content). This relation is closer to the earlier values of Kohman<sup>7</sup> and of Dufraisse and his collaborators<sup>8</sup> than to the more recent values of Kemp and Ingmanson<sup>9</sup> and of Cramer, Sjothun and Oneacre<sup>10</sup>. In all probability, the comparison of the mixture plays a part in the phenomenon, and this merits a separate study in itself.

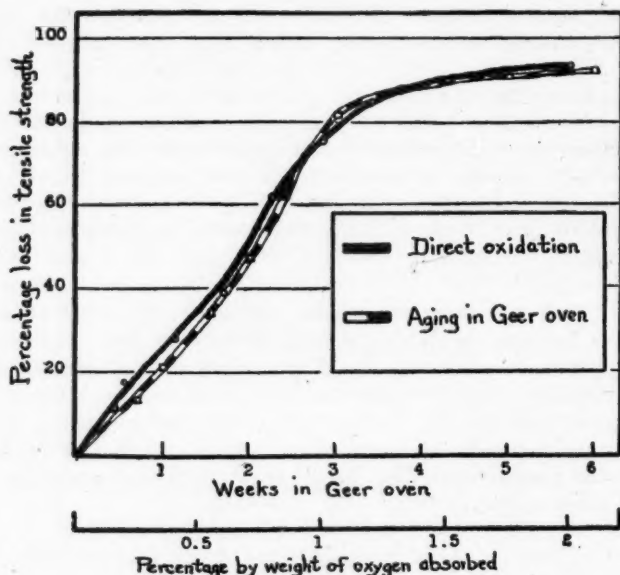


FIG. 1.

## CLASSIFICATION OF A SERIES OF MIXTURES

Since, as has just been shown, there is a close relationship between the rate of deterioration in a Geer oven at 70° C and the rate of oxidation in oxygen, it seemed of interest to determine the relative order in which the two testing methods would place a series of mixtures of different compositions.

The measurements which are about to be described were made on fine mixtures, which were kindly furnished by various manufacturers and of which only the characteristics in Table V can be given.

TABLE V

Mixture	Type of rubber and percentage	Sulfur content (percentage)	Type of mixture
A.....	Smoked sheet ..... 61	1.35	Carbon black loading.
B.....	First latex crepe..... 57.5	2.85	Loaded white.
C.....	First latex crepe..... 96.3	1.50	"Pure gum".
D.....	Smoked sheet ..... 66.2	1.30	Kieselguhr loading.
E.....	Smoked sheet ..... 70	1.75	Carbon black loading.

Aging of the samples in the Geer oven at 70° C was continued until they had deteriorated at least 50 per cent. The usual period of two weeks would not have been enough to distinguish clearly between mixtures B, C and D. Table VI and Figure 2 give the results of these measurements.

In a separate series of tests, samples from the five mixtures were cut into small parallelepipeds of the approximate dimensions 2×2×3 mm. in each case. The weights taken were 1.64 grams of A, 2.29 grams of B, 1.04 grams of C, 1.51 grams of D and 1.43 grams of E, which correspond to 1 gram of rubber in

each case. The heating unit was maintained at  $120^{\circ}\text{C}$ , and the measurements are given in Table VII and graphically in Figure 3.

It will be seen that the five mixtures were ranked in the same order by the two tests. The rates of oxidation of mixtures C and D were almost the same, and this is in accord with the fact that these two mixtures deteriorated at practically the same rate during the first weeks in the Geer oven. Likewise

TABLE VI

Loss in tensile strength after aging in Geer oven  
(percentage)

Mixture	1 week	2 weeks	3 weeks	4 weeks	5 weeks	6 weeks	7 weeks	8 weeks	9 weeks	10 weeks
A .....	48	65	80	82	85	—	—	—	—	—
B .....	14	32	45	56	65	—	—	—	—	—
C .....	17	23	35	48	56	71	—	—	—	—
D .....	16	25	31	34	36	38	48	56	69	—
E .....	—	—	—	10	17	25	—	44	50	58

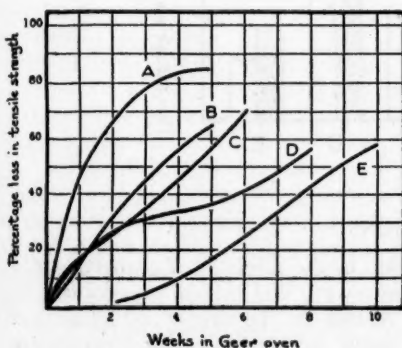


FIG. 2.

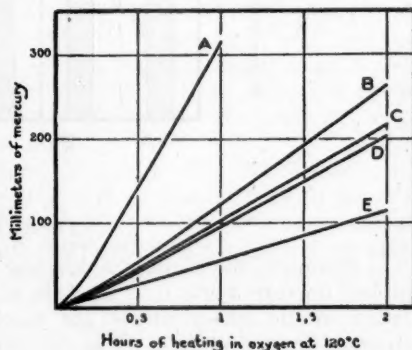


FIG. 3.

TABLE VII

Ascent of mercury (in mm.) after heating in  
oxygen at  $120^{\circ}\text{C}$

Mixture	0.5 hr.	1 hr.	1.5 hrs.	2 hrs.
A .....	141	313	—	—
B .....	54	127	190	265
C .....	48	108	160	218
D .....	47	60	153	220
E .....	27	103	86	116

the considerable differences in the rates of oxidation of mixtures A, B and E are reflected in the considerable differences in the aging curves for the Geer oven.

To show the similarity in the results in a more striking way, the oxidizability of each mixture (expressed as the ascent of mercury in the manometric tube after oxidation for 1 hour at  $120^{\circ}\text{C}$ ) and the relative loss of tensile strength of each mixture (after 4 weeks in the Geer oven) are shown in Figure 4.

The parallelism is quite satisfactory, and shows that a comparison of two mixtures by an oxidizability test of one hour in the manometric apparatus is just as reliable as a comparison by means of 4 weeks in the Geer oven.

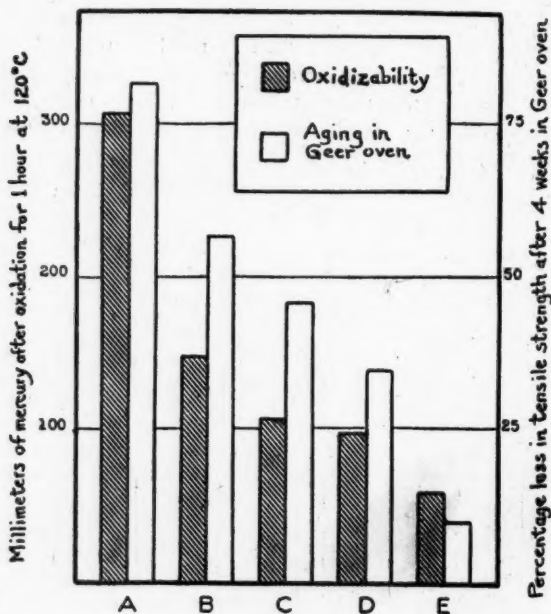


FIG. 4.

## CONCLUSIONS

In summary, the changes which take place in the mechanical properties of a rubber mixture when it is aged in a Geer oven, and which are evident by dynamometric measurements, are closely related to the proportion of oxygen absorbed by the sample. It is therefore much more practical and convenient to measure its oxidizability after only a few minutes' aging, using a sample of any shape whatsoever, and a weight of approximately one gram.

As far as any particular standard industrial mixture is concerned, there is no good reason for not conforming to the customary practice of rubber technologists of expressing aging on the basis of loss in tensile strength. In this case the only thing necessary to do is to calibrate the manometer in kg. per sq. cm. after having established the curve relating oxygen absorbed to loss in tensile strength.

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# SOME CONSEQUENCES OF THE ELECTRICAL DOUBLE LAYER IN RUBBER TECHNOLOGY \*

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The effects of the electrical double layer in connection with rubber manufacturing processes have, in recent years, become of rapidly increasing technical importance.

In the last two decades remarkable developments have occurred in the application of aqueous dispersions of rubber, or of rubber-producing materials. The characteristics of these dispersions are largely dictated by the electrical double layer and adsorbed material associated with it. These aqueous dispersions may be of several distinct types, viz.: (1) natural dispersions of natural rubber, in particular the latex of *Hevea brasiliensis*; (2) artificially prepared dispersions of natural rubber; (3) dispersions of artificial or synthetic rubber in which the rubber-like material has been formed from predispersed parent material; (4) artificially prepared dispersions of artificial or synthetic rubber. It is convenient to discuss these in substantially the reverse order to that in which they have just been enumerated.

Artificially prepared dispersions of synthetic rubber-like materials are latex-like fluids which can be applied in the same way as natural latex to manufacturing purposes, and not only impart any advantageous features of the dispersed material, but also possess a potential advantage in that dispersing agents can be selected which are resistant to attack by, or to growth of, bacteria or moulds, with consequent enhancement of stability, or which are favorable to the water resistance of the final product.

Selection of the dispersing agent is also possible in the production of artificial dispersions of natural rubber, but in this case protein from the original latex is also normally present and retains its tendency to gradual chemical change under the influence of hydrolytic agents introduced, for example, with the preservative, or arising in the form of enzymes.

Of the synthetic rubbers which have attained commercial production in the last few years, the best known are produced initially as dispersions or latices. Neoprene is obtained by the polymerization of a stabilized aqueous dispersion of chloroprene:  $\text{CH}_2:\text{CCl}\cdot\text{CH}:\text{CH}_2$ . The electrically charged layer responsible for the stability of the parent dispersion persists in the resulting dispersion of the polymerized material. The forms of Buna synthetic rubbers distinguished by a letter, e. g., Buna N and Buna S, are also derived by the polymerization of aqueous dispersions containing butadiene. In addition to butadiene, the parent dispersion contains also a second polymerizable substance (acrylic nitrile and styrene, respectively) and in each case copolymerization, or interpolymerization, occurs, with formation of long molecules in which nuclei of both types are associated in chain-like formation. The properties of the resulting homogeneous products are distinct from those of products obtained by polymerization of the parent substances singly, and subsequent mixing of the polymerized dispersions.

\* Reprinted from the *Transactions of the Faraday Society*, Vol. 36, Part 1, No. 225, pages 264-271, January 1940.

The nature of the adsorbed film influences the rate and result of the polymerization process<sup>1</sup> indeed the extensive patent literature includes numerous instructions as to the selection of appropriate stabilizing or protective colloids for the primary dispersions.

In the foregoing types of dispersions of rubber-like material, the electrical double layer is such that the globules normally exhibit the behavior of negatively charged particles. Qualitatively, therefore, their electrophoretic behavior is similar to that of natural *Hevea* latex, concerning which scientific investigation of the electrical double layer, and its related phenomena, is fuller.

Contrary to an almost natural assumption, the formation of rubber articles by electrodeposition of rubber from latex, as practiced in the well-known "Anode" process, is not electrophoretic in character. The rubber deposit is formed essentially by coagulation of the latex at the surface of a zinc anode (by zinc ions formed threat by the current) or at the surface of a porous membrane surrounding the anode (by ions migrating from the anode space which contains an appropriate solution, *e. g.*, of a calcium salt). An electroosmotic effect, however, is observable in the tendency of the wet deposit formed, with continued passage of the current, to act as a capillary membrane and to lose water by electroosmosis.

Quite recently the electrical behavior of the rubber globule has been applied to the production of concentrated latex by a procedure parallel to that adopted by Pauli and his coworkers for the separation of hydrophilic colloids into layers of low and high concentration, respectively, by carefully controlled electrodiagnosis or electrodecantation. In the process as applied to *Hevea* latex<sup>2</sup>, the electrophoretic movement is caused not only to effect localized concentration of the latex but also, by occasional short reversals of the potential, to prevent permanent attachment of rubber particles to the membrane. The concentrated latex separates gravitationally to form an upper stratified layer which can be separated mechanically and continuously.

In natural *Hevea* latex it can be shown by careful observation of the electrophoretic migration of the rubber particles that the adsorbed film, with which the electrical double layer is associated, normally consists of protein<sup>3</sup>. Incidentally it may be remarked that the coagulation phenomena of *Hevea* latex generally are well known to show a notable parallelism with the behavior to be expected of a not very highly hydrated protein substance. The amphoteric nature of the rubber protein renders it possible, by reduction<sup>4</sup> of the pH to give the rubber particles in *Hevea* latex a positive electric charge instead of the original negative one. A similar effect can be obtained by addition of multivalent cations, *e. g.*, of thorium<sup>5</sup> or by addition of a cationic soap, *i. e.*, a substance giving rise to a colloidal positive ion. With latex so treated, cathodic deposition can be effected, whereas normally the electrodeposition of rubber is anodic. Although there are differences of opinion, such evidence as there is available indicates that the colloidal particle in rubber latex is relatively slightly hydrated<sup>6</sup>. Indeed, the difficulty which is experienced in the complete removal of the adsorbed protein by repeated dilution and concentration by removal of part of the aqueous phase gives some indication of denaturation accompanying adsorption, so that the latter process is not completely reversible.

Investigation of the nature of the electrophoretic behavior of the rubber particle of preserved *Hevea* latex<sup>3</sup> has indicated that, under special conditions of dilution and of pH, the adsorbed film may not consist entirely of protein, and that the fatty acid soap in the latex may form part of the surface layer.

Replacement of the protein layer by a film of other composition is possibly more definitely demonstrated by the alteration in the isoelectric point of the latex globules when certain other protective colloids are added<sup>7</sup>. In these circumstances the normal protein can become so effectively displaced that the dispersed particles show no sign of inversion of electric charge even at a pH value of 2, whereas normally the isoelectric point occurs at a value of approximately 4.5. Reference has already been made to the indications that the protein layer is probably in a partly denatured condition, so that the reversibility of its adsorption and complete displacement of the protein may be affected.

Recent investigations<sup>8</sup> have suggested that the protein of preserved *Hevea* latex is not a single substance, but comprises two proteins of distinct isoelectric value, viz., 4.5 and 3.9. It appears uncertain whether these values represent two different proteins in the original latex, or whether either corresponds with a partial degradation product of the original protein.

Spontaneous coagulation of *Hevea* latex has been observed at much higher values of pH than the value normally associated with the coagulation phenomenon. This observation likewise may have an explanation in the hydrolysis of the adsorbed protein, *e. g.*, by enzyme influences, with formation of amino acids such as arginine, which is known to be present in the hydrolysis products of rubber protein<sup>9</sup>, and which has an isoelectric point at pH approximately 10. It may be only a coincidence that guanidine, the nucleus of which is present in the arginine molecule, can itself act as a coagulant for latex under certain conditions<sup>10</sup>.

A set of observations with dialyzed *Hevea* latex gives interesting additional information on the electrical behavior of the rubber globule. If a series of portions of ammonia-preserved latex are subjected to graded alteration in pH, it is found that coagulation occurs over a range from 5.75—2. If, on the other hand, the same latex has first been submitted to dialysis through a collodion membrane, the range of coagulation is much less wide; so sharp indeed is the coagulation point (pH approximately 4.3) that unless the addition of acetic acid is effected cautiously it is easy to overshoot the isoelectric point, and to pass unintentionally to the condition of a stable positive latex. This result has a possible parallelism in the observation that purification of *Hevea* latex "by centrifuge and (or) by dialysis" facilitates the avoidance of coagulation when a cationic soap is added for reversal of the electric charge on the rubber particles<sup>11</sup>.

In our experiments the latex in each case was diluted to a dry rubber content of 12 per cent, and 10 cc. portions of each were run into a series of glass tubes. To each set various quantities of diluted acetic acid were added followed by vigorous stirring. After two hours, the clots were removed, washed, sheeted, dried for twenty-four hours at 100° C and weighed. The pH values of the sera were determined by means of the glass electrode.

The latex examined was derived from one lot of ammonia-preserved latex by the various treatments indicated below.

(A) Normal ammonia-preserved latex.

(B) The latex which had been treated with formaldehyde to remove the ammonia.

(C) The latex which had been dialyzed against distilled water for three days.

(D) Dialyzed latex (C) to which had been added potassium sulfate to give a final concentration 0.1 *N*.

(E) Dialyzed latex (C) to which had been added ammonium acetate to give a final concentration 0.1 *N*.

The results, plotted in Figures 2 and 3, show that both dialysis and treatment with formaldehyde have the effect of reducing the pH range over which coagulation takes place. The pH value at which maximum coagulation occurs is

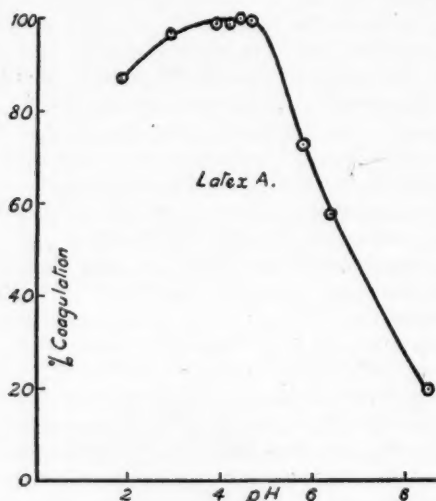


FIG. 1.

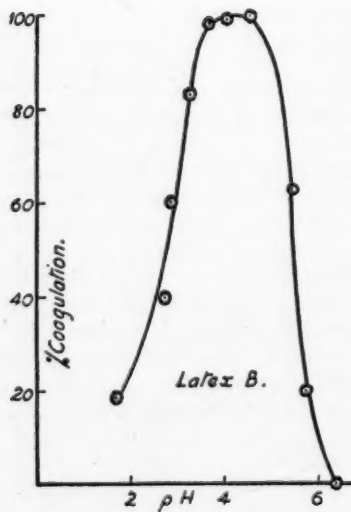


FIG. 2.

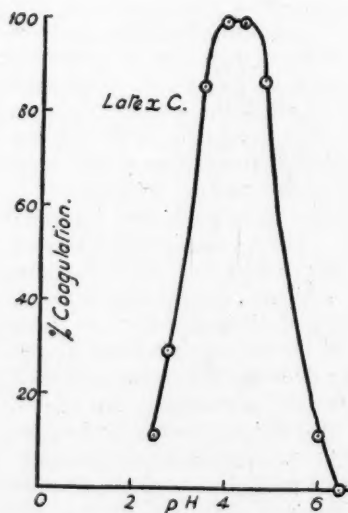


FIG. 3.

more definite with dialyzed latex than with formaldehyde-treated latex, the difference being due, most probably, to the removal by dialysis of ions other than the ammonium ion.

The addition of a small quantity of ammonium acetate or potassium sulfate to the dialyzed latex causes coagulation again to take place over a wide pH range (Figures 4 and 5).

The greater range of pH over which coagulation occurs with normal ammonia-preserved latex than with the same latex after dialysis is, therefore, attributable to the presence of saline substances, derived from the ammonia and from the serum. This result is in accord with the knowledge that salts broaden the range of pH over which coagulation of a protein can take place and that, in the absence of salts, the coagulation pH of the protein is more critical<sup>12</sup>. The observed influence of dialysis on the coagulation behavior consequently provides additional evidence of the existence of a protein layer on the rubber particles in *Hevea* latex.

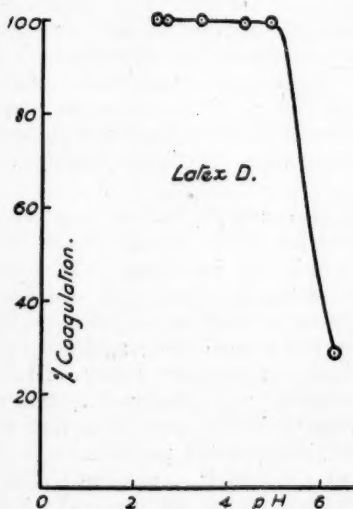


FIG. 4.

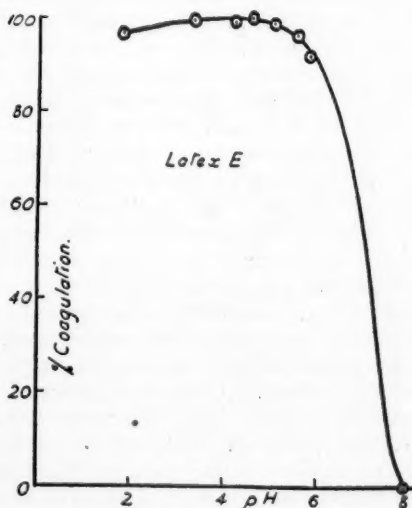


FIG. 5.

This effect of the natural saline components of the serum on the coagulation of latex by acetic acid may occur by way of combination of their ions with ionized groupings of the protein, with formation of undissociated groupings and consequent reduction in total charge on the protein. The effect may take place on both sides of the isoelectric pH, combination being between positively charged protein molecules and negatively charged ions from the saline substance in more acid media, and between negatively charged protein molecules and positively charged ions from the saline substance in more alkaline media. The charge acquired by a protein molecule at pH values on either side of the isoelectric pH is therefore less, and the coagulation range greater, in the presence of soluble salts. It can be inferred from experiments which measure the combination of ions with gelatin<sup>13</sup> that this effect in the reduction of the charge is more marked on the alkaline side of the isoelectric pH than on the acid side. Adsorption phenomena between the charged protein and the appropriate ions of the saline substances present could also lead to this type of influence on the coagulation behavior. The effect in either case would appear to be analogous in origin to



the well-known coagulant effect of extraneous multivalent ions, *e. g.*, of zinc (see p. 263) or aluminum.

The marked ability of some colloidal substances, *e. g.*, sodium alginate, gum tragacanth, etc.<sup>14</sup>, to accelerate the creaming of *Hevea* latex, and its dependence in some cases on the presence of an additional colloidal substance without creaming activity, are other effects which are probably related to the activity of an adsorption layer at the surface of the dispersed rubber particles.

As has already been mentioned, the component of normal latex which is mainly responsible for the formation of the protective layer on the dispersed rubber particles is of protein character. In the preparation of ordinary forms of rubber, such as pale crepe rubber or smoked sheet, the protein remains associated with the rubber and constitutes approximately 2 or 3 per cent of the dry material, where its presence causes impairment of the water resistance of the rubber hydrocarbon. Effective displacement of the protein layer (and exclusion of surplus protein dissolved in the serum) by other adsorbed layers of less hydrophilic material, for the production of natural rubber with high resistance to water absorption, therefore, still constitutes a problem. Complete solution of this problem appears to be hindered by partial denaturation undergone by the adsorbed protein layer. The most effective procedure hitherto has been by a creaming process repeated several times, possibly combined with a process of creaming by centrifugation.

It is a well known fact in rubber technology that the physical and mechanical properties of rubber, such as tensile strength and resistance to abrasion, to tearing and to solvents, can be profoundly modified by the incorporation of certain finely divided substances in the rubber. The actual mechanism by which this so-called reinforcing effect is produced is a problem which still awaits complete elucidation. It has generally been accepted that a reinforcing agent exerts a greater effect the more intimate its degree of dispersion in the rubber, and that the interfacial energy and the intensity of wetting in the dispersed system are important factors, with which must be associated, in the most important case of carbon black, the adsorbent power of the incorporated particles. The full reinforcing effect is, however, not immediately developed; a mixture of masticated rubber and carbon black (containing for example 20 per cent of the latter) may be completely soluble in ordinary rubber solvents initially, but on storage for a few days it becomes tough, resistant to tearing and insoluble<sup>15</sup>. Recently indications have been obtained that the reinforcing effect is enhanced if a rubber—carbon black mixture, before vulcanization, is subjected to a heat treatment<sup>16</sup>, *e. g.*, at 132° (and remilling), and that this alteration in the effect arises from some form of flocculation of the dispersed particles of carbon black in the temporarily softened rubber. The result may be likened to the formation of a gel from an aqueous dispersion of a colloidal clay. The desirable flocculation which is believed to underlie the increase in reinforcing effect can also occur during the heating period necessary for vulcanization<sup>17</sup>, and so is favored by retardation of the vulcanization process by means other than the lowering of the temperature. A favorable influence can be exerted also by the presence of small proportions of certain substances such as cetyl pyridinium bromide and lauryl pyridinium sulfate, which, in spite of an accelerating effect on vulcanization, appear to assist the flocculation process.

The probable importance of the adsorptive action of carbon black in these reinforcement phenomena is emphasized by the observation that previous removal of the natural fat acid components of rubber (by acetone extraction)

renders the satisfactory dispersion of carbon black in the rubber, by milling, more difficult, but that incorporation of stearic acid restores the facility of dispersion<sup>18</sup>. Indeed a tentative calculation has indicated that the maximum proportion of carbon black which can be effectively dispersed in rubber corresponds approximately with the quantity for which the natural fat acids of the rubber suffice to form an unimolecular surface layer<sup>19</sup>.

Possibly some light is thrown on this phenomenon by an investigation of the behavior of dispersions of carbon black particles in organic media other than rubber.

Although it is possible to make an apparently stable dispersion of carbon black in rubber by the customary drastic milling or mixing operation, the apparent stability of the resulting dispersion probably arises largely from the viscous character of the medium. Such a mechanically prepared mixture of rubber and carbon black (with a low proportion of the latter) can also be dissolved in benzene to give a dispersion of considerable degree of permanence which is probably attributable again to the same cause. On the other hand it has not been found possible to produce a permanent dispersion of carbon black in benzene or in a solution of rubber in benzene by prolonged grinding, *e. g.*, in a pebble mill, without any additional colloid material, flocculation occurring spontaneously, almost at once in the former case and more slowly in the latter.

It appears probable therefore that mechanically prepared dispersions of carbon black in rubber are inherently unstable and that, although flocculation may be so slow as to be inappreciable at ordinary temperatures, flocculation will always set in when the conditions of temperature, and consequently reduced viscosity of the medium, permit the necessary movement of the particles. With aniline (dielectric constant 7.3, dipole moment  $1.56 \times 10^{-18}$  e.s.u.) as dispersion medium, it is possible in a pebble mill to produce a semistable dispersion of carbon black, flocculation of which is observed only after several days, whereas with nitrobenzene (dielectric constant 34, dipole moment  $3.9 \times 10^{-18}$  e.s.u.) the resulting dispersion is stable. It seems reasonable therefore to assume that the dielectric constant of carbon black is so near that of benzene (2.3) and of rubber (2.2) that the electric charges resulting from contact of the particles with these media are too small for the dispersions to show permanent stability. Orientation of the polar molecules around the charged particles may lead to a further increase in the stability of the dispersions in nitrobenzene or aniline. Cetyl pyridinium bromide also causes the flocculation of an otherwise stable dispersion of carbon black in nitrobenzene. The unstable dispersion of carbon black in benzene is not observable affected by cetyl pyridinium bromide.

It can be shown that in an electric field carbon black particles dispersed in benzene or nitrobenzene tend to move toward the anode, but the main effect is a formation of continuous strings of particles reaching out from the electrodes particularly from the anode; oscillation of isolated particles from electrode to electrode may also be observed, especially in benzene. These results of ours appear to be comparable with the well-known Lodge-Cottrell effect, and are probably explained by the high electrical conductivity of the dispersed material and the low conductivity of the dispersion medium. They are also in accord with an earlier observation that carbon black contains isotropic and anisotropic particles<sup>20</sup>. With cetyl pyridinium bromide present, the results are somewhat different, the movement of the particles indicating a swirling of the liquid, while the stringing of the particles is less pronounced. Dispersions of carbon black in rubber itself also give evidence of such stringing of the par-

ticles. Application of a pulsating electric potential induces rapid increase in the electrical conductivity of the dispersion, i. e., of the compounded rubber, and the effect is accentuated by the presence of cetyl pyridinium bromide and similar substances.

We have to express our indebtedness to the Dunlop Rubber Company, in the Chemical Research Department of which the new experiments here incidentally recorded were made.

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# DISPERSION OF PIGMENTS IN AQUEOUS MEDIUM \*

## I. MECHANISM AND EVALUATION OF DISPERSING AGENTS

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Surface-active compounds have become indispensable ingredients in latex technology. This chemical group comprises all wetting and dispersing agents, protective colloids, most other stabilizers, cationic soaps used in producing positively charged latex, etc. Although these agents have certain features in common, there are essential differences in the functions they fulfill and in the mechanism they employ. These differences are not always observed clearly. A distinction between wetting and dispersing agents, for instance, is sometimes not recognized because there are cases where one chemical combines both functions. In spite of these cases, which are exceptions rather than the rule, it seems important to distinguish wetting from dispersion for a successful application of these agents.

### RELATION OF WETTING, DISPERSING AND PROTECTING AGENTS

A wetting agent is a material which is soluble in water and which in small quantities will materially reduce the surface tension of water. The reduction in surface tension is the most important factor in replacing the gas phase adsorbed on the surface of solids by the liquid phase. The lower the surface tension, the better, as a rule, is the wetting power. Size and shape of the wetted surface are of no importance. Whether one large surface is to be wetted or a number of small articles which may either be single and independent or loosely or irreversibly combined makes no difference.

The wetting agent is not intended to cause any change in the state of agglomeration or dispersion of the particles. Where agglomerates are temporarily broken up mechanically in the presence of a wetting agent, they will reform as readily as though no agent were present. Where a wetting agent does affect the state of subdivision of the discontinuous phase, the effect is secondary. This can be a dispersing effect, one of the rare cases of a combination wetting-dispersing agent. More often the wetting agent itself or some impurity present detrimentally affects the dispersion, *i. e.*, causes agglomeration or flocculation, but this does not diminish its value as a wetting agent. Wetting agents are known in great number; while there are relatively few true dispersing agents known.

In general dispersing agents do not reduce the surface tension of water to a marked extent and, therefore, do not materially improve the wetting power of the solution. If they do, it is merely incidental. The function of an aqueous dispersing agent is to deflocculate loose combinations of particles (usually by assistance from an outside mechanical force). Deflocculation means that all loosely aggregated particles in the flocs become completely independent of each other. This is achieved by overcoming the adhesion forces existing be-

\* Reprinted from the *India Rubber World*, Vol. 101, No. 3, pages 50-52, December 1, 1939; No. 4, pages 33-37, January 3, 1940.



tween particles; these forces are the cause of agglomeration or flocculation. Flocculation is a common behavior of microscopic particles in suspension. As a rule, particles of lyophobic character show stronger adhesion, *i. e.*, more flocculation, than lyophilic particles. Therefore, dispersing agents show the greatest effect with highly flocculated hydrophobic systems. Lyophilic particles tend to disperse by themselves to some extent; therefore the effect of dispersing agents, even when producing complete deflocculation, is less spectacular in such systems.

A dispersing agent is not able to subdivide a homogeneous phase or to overcome such strong adhesion as exists in coagulated latex, for example. To redisperse such systems, mechanical force is necessary.

The term "dispersing agent" is sometimes used to designate substances which are instrumental in mechanically disintegrating a homogeneous phase or a coagulum. Glue and bentonite belong to this group when used to make artificial latex from rubber or to produce asphalt dispersions. They should be more properly called "disintegrating agents".

A third kind of dispersing agent is that used to disperse a discontinuous solid phase in a continuous plastic phase. This represents an entirely different problem. The function of this type of dispersing agent is to reduce the amount of mechanical energy necessary to disperse the solid in the plastic phase. This is accomplished, it is believed, by the reduction of surface tension of the plastic, which makes this kind of dispersion resemble more a wetting than a dispersing mechanism. The dispersion of carbon black in rubber with stearic acid as the dispersing agent is an illustration of this type of dispersion. This paper is not concerned with such cases.

According to the above, the essential difference between a wetting and a dispersing agent lies in the fact that the former primarily changes the character of the liquid so that the contact angle with the solid is substantially reduced, while the latter directly changes the character of and is adsorbed at the liquid-solid interface. Dispersing agents do not function unless they are adsorbed on suspended particles. Owing to the polar-nonpolar character of dispersing agents, the affinity of their molecules toward hydrophobic particles is stronger than toward hydrophilic particles. In other words, the adsorption equilibrium is more favorable with hydrophobic than with hydrophilic surfaces, which is an additional reason why dispersing agents are more effective with hydrophobic particles.

The foregoing makes it understandable why the action of dispersing agents is so specific, *i. e.*, why they are extremely efficient for some pigments, while completely ineffective for others. Wetting agents, influencing merely the liquid phase, have been found to be much less specific toward different pigments.

To obtain dispersion, the adhesion forces between the particles must be reduced at least to a certain critical value where the Brownian movement becomes equal to or stronger than adhesion. The degree of dispersion increases as the repelling forces increase beyond the point of equilibrium.

Protective colloids, such as proteins, glue, starch, agar, etc., form a third group of surface active compounds, different from the other two groups, although they sometimes may show dispersing or wetting properties in addition to their protective qualities. This condition does not make them identical either to the wetting or to the dispersing agents. Their mechanism resembles that of dispersing agents only insofar as their effect is centered on the solid-liquid interface.



Protective colloids are characterized by very large hydrophilic molecules in which the hydrophilic or polar groups are generally distributed more or less at random. The molecules of dispersing agents, on the other hand, are of polar-nonpolar structure, with the polar groups concentrated at one section of the molecule, causing orientated adsorption.

A true dispersing agent is not of pronounced hydrophilic nature. A dispersion produced with such agents will generally follow the rules governing a hydrophobic system. A protective colloid, on the other hand, is strongly hydrophilic, and gives the particles on which it is adsorbed a decidedly hydrophilic character. A dispersion produced with protective colloids will obey the rules governing hydrophilic systems. By the addition of protective colloids the adhesion forces between the particles may or may not be reduced, depending (1) on the nature of the protective colloid, and (2) on the original adhesion between the particles themselves. But even if adhesion may increase with the addition of a protective colloid, the stability of the dispersion increases<sup>1</sup>. Such a system will not be easily flocculated or coagulated by electrolytes. In cases where adhesion forces are reduced by the presence of protective colloids, the system will still not behave as if dispersed by means of a true dispersing agent. This becomes apparent when observing the difference in properties of two liquid-solid systems, one produced with a protective colloid and the other, a dispersing agent. For instance, the viscosity of concentrated pastes will be higher when made with protective colloids than with dispersing agents.

The simultaneous use of protective colloids and dispersing agents should be avoided if possible, since complications arise, owing to competing adsorption, which impair the effectiveness of both materials. Likewise, where wetting agents must be used with dispersing agents, utmost care has to be exercised in their selection in order to preserve both effects fully.

#### TESTS FOR DEGREE OF DISPERSION

In the evaluation of dispersing agents it is important to be able to ascertain how nearly the ideal state of dispersion is approached. There are several known methods of testing for the degree of dispersion. Among these are: microscopic observation; filtration behavior; transparency; sedimentation; consistency; and outward appearance. These tests are briefly reviewed below, and in the second part of this paper a new method for quickly recognizing dispersing agents of high effectiveness will be presented.

#### MICROSCOPIC TECHNIQUE

Microscopic observation may be carried out either under reflected or transmitted light. The former method is simpler, but of limited value, as it does not show the particles dispersed in the continuous phase. A paste is made of liquid and solid phase and is dried out. The smoother the resulting film and the finer its grain, the better is the dispersion, according to this test. Observation under transmitted light is carried out in extreme dilution of the solid phase and requires certain precautions for two reasons.

(1) Adsorption of the dispersing agent from the solution is a matter of equilibrium and, therefore, an amount of dispersing agent ample at normal pigment concentration may become insufficient at a high degree of dilution, with the result that partial flocculation sets in.

(2) An actually well-dispersed system may appear flocculated because of imperfect technique when diluting. No matter how slowly and carefully the water is stirred in, the higher viscosity of the concentrated pigment dispersion makes it very difficult to distribute that phase uniformly throughout the phase of lower viscosity. Some large and a good number of small specks will remain. These break up only when the cover glass is pressed down on the slide, or, preferably, when the cover glass is slightly rotated on the slide. This should always be done before judging the state of dispersion. Generally, true agglomerates or flocculates will not be broken up by this manipulation, but if they do break up the single particles will recombine quickly as the result of Brownian motion.

Where due care is exercised in carrying out the test, this method is the best and most direct way of evaluating dispersion. It gives reproducible results which can be permanently recorded by microphotographs.

#### THE FILTER TEST

Ordinary qualitative filter paper retains flocculates with little or no loss. Hence the filtrate of an undispersed suspension shows little or no color of the solid phase. Dispersed particles of the fineness of ordinary pigments (between approximately 0.2 and 2.0 microns) will pass through the filter. The higher the percentage of dispersed particles, the more opaque will be the filtrate. A colorimetric comparison will give a good indication as to the degree of dispersion of a certain system. A more quantitative result is obtained by a dry solid content determination of the filtrate, which gives directly the percentage of dispersed pigment.

#### TRANSPARENCY

A dilute, well dispersed suspension of pigment in a test-tube is quite clear and transparent, and will not show an opaque ring at the air-glass-liquid interface. A flocculated or partly flocculated suspension of equal strength will be somewhat opaque and will leave the glass wall slightly stained. This condition is because adhesion forces not only exist between the suspended particles, but also between the particles and the glass wall, to which the particles may adhere upon contact.

#### SEDIMENTATION TESTS

Obedying Stokes' Law, a flocculated system settles rapidly, leaving a clear layer of water on top, with a sharp demarcation line between the water and the suspension. The sediment (or cream, if the particles are lighter than water) occupies a comparatively large part of the total volume. The particles in a dispersed system settle very slowly, and no sharp line of demarcation is exhibited between the water layer and the suspension layer for a relatively long time. But once the particles have settled, they occupy a very small volume. This state is due to the fact that, on settling, single particles pack very closely. Flocculates, on the other hand, with their highly irregular, semi-rigid structure, occlude much water, especially if the particles are not spherical and therefore occupy a greater volume. The arrangement of the particles in the dispersed and the flocculated sediment may be compared to the piling of bricks—thrown together at random in the case of the flocculated sediment and laid orderly together as in a brick wall in the case of the dispersed sediment.

These tests are best carried out in calibrated graduates with ground glass stoppers, for example in 10 cc. graduates with 0.1 cc. divisions. Usually, good results will be obtained by using 0.25 cc. of the pigment with 9.75 cc. of the water containing the dispersing agent. Care must be taken that all graduates are shaken in the same manner and for an equal length of time; otherwise the results will not be reliable or reproducible.

This method allows a fairly good comparison of the efficiency of different dispersing agents, and also indicates rather accurately the least amount of dispersing agent required to obtain maximum dispersion.

#### CONSISTENCY

If a flocculated system is characterized by a large volume of sedimentation and a high amount of mechanically occluded water, it follows that the act of dispersing a flocculated suspension must be accompanied by strong liquefaction. It will always be found that systems of the consistency of flocculated, filter pressed, stiff pulp become liquid on the addition of effective dispersing agents. Thus a much higher concentration of pigment can be obtained when a dispersing agent is used. As a rule it can be said that the better the dispersion, the higher will be the concentration of pigment obtainable at a certain consistency—although this statement does not always hold at extremely high concentrations.

#### OUTWARD APPEARANCE

Flocculated pastes exhibit flat, dull, and rough surfaces; whereas dispersed suspensions or pastes produce a glossy and perfectly smooth film. Furthermore flocculated pigments tend to form pastes, showing definite yield values over a very broad range of concentration; while dispersed systems will flow even at high concentrations.

## II. INDUCED DILATANCY AND ITS RELATION TO DISPERSION

The first part of this paper discussed wetting, dispersing and protecting agents and the various known methods of evaluating dispersing agents. In this second part a new dispersing agent will be compared with other representative agents of this type, and a new method of determining the degree of dispersion based on dilatancy will be presented.

#### SEDIMENTATION TESTS ON FOUR DIFFERENT DISPERSING AGENTS

The new agent, "Hornkem," designated as agent A, is a colloidal, sulphonated derivative of vegetable origin, processed and purified by a special process. The structure of its molecule is unknown. Agent B is identical with agent A except that it has not been purified. Agent C is a polymerized organic salt of a sulphonic acid of alkyl-aryl type; while agent D is a dispersing agent of the glucoside type.

The dispersing power of these four agents for zinc oxide was determined by the sedimentation volume method: 1.42 grams of zinc oxide (Red Seal, Anaconda), having a displacement volume of 0.25 cc., and 9.75 cc. of solution of the different dispersing agents in varying concentrations were shaken vigorously for 30 seconds in glass stoppered graduates with 0.1 cc. divisions. After standing undisturbed, the volume of sediment at different periods was observed and recorded in Table I.

With no dispersing agent present, the volume of sediment was found to be large. After one day's settling the upper layer was perfectly clear, and thereafter the volume of sediment slowly decreased until it had reached a constant value after the fourth day. With agent A, there was very little sediment at the end of 24 hours, and the upper layer was extremely cloudy. As the suspended zinc oxide particles slowly settled, the volume of sediment increased, but did not become constant until after complete sedimentation.

It appears from Table I that there exists an optimum concentration of agent A at which the dispersing effect is at a maximum; above as well as below this optimum value, dispersion is not so pronounced. Agent B shows this same behavior; with concentrations of 24% and 12% of agent B a clear top layer was obtained after 24 hours. At all other concentrations, however, cloudiness prevailed for several days. With 0.08% dispersing agent, some flocculates

TABLE I  
VOLUME OF SEDIMENTATION

Concentration of dispersing agent	Number of days of settling						
	1	2	3	4	5	6	7
	Cc. of sediment after settling						
No Agent .....	8.60	8.50	8.50	8.3	8.3	—	—
Agent A ..... 11.00%	1.10	1.29	1.36	1.41	1.46	1.49	1.49
2.80%	1.18	1.31	1.38	1.39	1.39	1.40	1.40
1.10%	1.18	1.31	1.35	1.38	1.38	1.40	1.40
0.56%	.90	1.10	1.18	1.19	1.20	1.20	1.20
0.28%	.91	1.12	1.20	1.20	1.20	1.20	1.21
0.07%	1.05	1.22	1.29	1.30	1.30	1.30	1.30
Agent B ..... 24.00%	3.56	2.10	1.79	1.70	1.69	1.65	1.65
12.00%	2.00	1.7	1.69	1.69	1.69	1.69	1.69
3.00%	1.65	1.65	1.65	1.66	1.65	1.65	1.63
1.20%	1.22	1.4	1.41	1.42	1.41	1.42	1.41
0.60%	2.00	2.01	2.01	2.01	2.01	—	—
0.30%	2.22	2.23	2.23	2.22	2.22	—	—
0.08%	2.60	2.55	2.55	2.55	2.55	—	—
Agent C ..... 2.90%	2.25	2.25	2.25	2.25	—	—	—
Agent D ..... 2.80%	3.90	3.90	3.90	—	—	—	—

were seen adhering to the glass wall. The smallest volume of sedimentation after seven days was 1.41 cc. for agent B, compared to 1.20 cc. for A. After the first day the difference was even greater; 1.22 cc. for B and 0.90 cc. for A.

In the case of agent C, cloudiness was observed after 24 hours' settling, but the quantity of suspended material at this time was not great enough to cause the volume to increase upon subsequent settling. The same was true for agent D. In the case of both C and D an excess of agent affected the degree of dispersion much less than in the case of A and B. For this reason Table I for C and D gives the sedimentation volume for one concentration only, which is believed to represent approximately the maximum.

In the light of this test, agent A clearly appears to be the most effective of the four agents concerned.

#### DILATANCY

While determining the maximum concentration of pigment obtainable with agent A by thoroughly mixing and kneading dry pigment and liquid with a



spatula on a glass plate, a peculiar phenomenon was observed. When the pigment concentration became very high, for example, 76% by weight of zinc oxide, the paste became glossy and free-flowing like heavy oil. Yet this liquid adhered tenaciously to the glass plate and offered tremendous resistance to any outside force attempting to move, agitate or dislocate it. The harder it was forced, the greater would be the resistance it offered. When an attempt was made to thrust a knife quickly into a large quantity, the material behaved like an elastic solid. The glossy mass became dull and rough in appearance where the knife struck the surface. Immediately after the knife thrust the material began to flow and leveled out, so that no trace of the indentation remained. This cycle could be repeated at will. When a spatula was quickly drawn over the material on a glass plate, a similar effect was observed.

Certain finely ground minerals such as diamond, quartz and glass, and a few other substances such as starch have been found to display such a behavior<sup>2, 3</sup> without dispersing agents present. Also, ordinary beach sand has been found to behave similarly<sup>4</sup>. This phenomenon has been termed "dilatancy".

Dilatancy has been associated with close packing of solid particles or their uniform distribution in a liquid medium. If there is just enough liquid present in a system to wet all particles when they are most closely packed, any disturbance of this arrangement must necessarily produce a less close packing of the particles, with the result that the water is drawn into the large interstices and the whole system turns dry and hard. If the cause of the disturbance is eliminated, the particles, under certain conditions, will return to their original position, either without the aid of outside influence or by tapping the container slightly. The behavior of the material in the former case is referred to as "active dilatancy" and in the latter case as "passive dilatancy".

#### NATURAL VS. INDUCED DILATANCY

To the best of the author's knowledge the above phenomenon has never been previously discussed in the literature in connection with dispersing agents. Dilatancy has always been understood to be an inherent property of certain minerals and other substances. No case has been reported before where, by the addition of a dissolved chemical, dilatancy has been artificially induced in a substance which by itself shows no trace of this property.

Naturally dilatant substances do not exhibit so marked a degree of this characteristic as can be obtained through the use of an effective dispersing agent; they are not so fluid, nor do they resist a change in particle arrangement to the extent that is found in induced dilatancy. This may be partly due to the fact that zinc oxide has strongly anisometric particles; whereas most naturally dilatant substances which have been investigated have more or less spherical particles<sup>5</sup>. It seems understandable that anisometric particles interfere more with each other than spheres do; hence the latter lend themselves better to dilatant behavior, the former to thixotropy. However, if an anisometric system can be made to pack closely, any disturbance in the packing is of greater consequence than with spherical particles. The dilatancy becomes more pronounced.

Because a pigment becomes both well dispersed and actively dilatant when treated with agent A, the existence of a close relation between these two phenomena is apparent. This relation had been assumed by Freundlich<sup>2, 3</sup> for naturally dilatant systems.



## RELATION OF PIGMENT CONCENTRATION TO DILATANCY, FLOCCULATION AND THIXOTROPY

The relation between pigment concentration on the one hand and dilatancy and flocculation on the other has been examined and is recorded in Figure 1. The maximum concentration of pigment obtainable with different amounts of agents A and B has been plotted. Active dilatancy takes place only in the approximate range indicated, *i. e.*, where the top curve is at a maximum. As the maximum concentration obtainable decreases, active dilatancy becomes less pronounced. Instead of flowing down a spatula rapidly and in thin strings, the mass flows slowly and in broad bands and, as the maximum concentration further decreases, the paste ceases to flow by gravity alone. In this state (passive dilatancy), slight tapping of the spatula is required to produce flow. The lower curve, representing agent B, at no point goes above the stage of passive

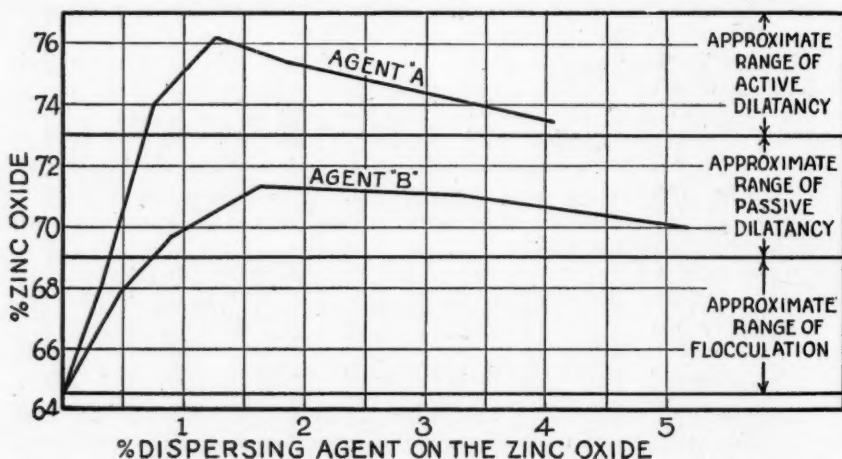


Fig. 1.—The relation of dilatancy and flocculation to maximum concentration in zinc oxide pastes at given percentages of dispersing agents A and B.

dilatancy. At a still lower maximum concentration the material passes into that state where it no longer displays dilatancy of any type, *i. e.*, will not flow even when agitated. Here the paste is completely flocculated. Further observations on the behavior of agent A are presented in Table II.

It was noted in these experiments that with relatively small amounts of agent A and at less than maximum pigment concentration, the system became distinctly thixotropic. This means that flocculation, thixotropy, passive dilatancy, and finally active dilatancy, must be regarded as various stages of dispersion with no sharp demarcation line separating one stage from the other.

Freundlich<sup>2</sup> correlates these factors as follows.

Dispersion is not mentioned in this connection at all; yet according to the evidence that has been presented, dispersion is the connecting link between all the properties mentioned. Close and loose packing are not to be regarded as opposing principles, but as the outer limits for the entire range of dispersion, from complete flocculation, to complete dispersion. All intermediate stages exist, and can be produced in flocculated systems of any type by the addition of the proper quantities of certain surface-active agents.

This relation, although recognized, has not been brought out quite as clearly before, because the gradual transition of a substance through the stages from flocculation to active dilatancy was unknown. There are probably few chemicals of such high efficiency as agent A, and most dispersing agents are not effective enough to produce systems exhibiting active dilatancy. For instance, agent B is capable only of producing systems that are passively dilatant, and agents C and D at best produce systems showing weak signs of passive dilatancy.

TABLE II

## EFFECT OF VARIOUS CONCENTRATIONS OF AGENT A ON PROPERTIES OF ZnO

1. For 5 g. ZnO—2.75 cc. water (no dispersing agent present) necessary to just make homogeneous paste.  
Description —Very stiff. With 5 cc. more it is still a paste, without a trace of passive dilatancy. On tapping a horizontally held spatula, material piles up instead of flowing down.
2. For 5 g. ZnO—2.45 cc. of 0.5% agent A solution necessary to just make a homogeneous paste.  
Description —No dilatancy. 1.1 cc. additional solution necessary to liquefy paste, which still does not flow because it is thixotropic, with very short time of solidification.
3. For 5 g. ZnO—2.19 cc. of 1% agent A solution necessary to just make a homogeneous paste.  
Description —Still appears like ordinary paste, but slightly passively dilatant. 0.4 cc. additional solution liquefies. Resulting product behaving as (2).
4. For 5 g. ZnO—1.77 cc. of 2% agent A solution necessary to just make homogeneous paste.  
Description —Distinctly passively dilatant. Liquefied by one more drop (0.04 cc.). Slightly thixotropic with much longer time of solidification than (2) and (3).
5. For 5 g. ZnO—1.56 cc. of 4% agent A solution necessary to just make homogeneous paste.  
Description —Very actively dilatant. Completely liquefied by one drop. No measurable thixotropy.
6. For 5 g. ZnO—1.63 cc. of 5.6% agent A solution necessary to just make homogeneous paste. Otherwise like (5).

TABLE III

Close packing	Loose packing
Small volume of sedimentation	Large volume of sedimentation
Dilatancy	No dilatancy
No plasticity	Plasticity*
No thixotropy	Thixotropy

## DILATANCY IN OTHER PIGMENT DISPERSIONS

Many pigments in addition to zinc oxide can be made actively dilatant. Among them are antimony oxide, lead carbonate, toluidine toner, chrome yellow and chrome orange. Results of sedimentation tests on chrome yellow dispersions are shown in Table IV.

Again agent A has the smallest sedimentation volume, *i. e.*, is the most effective dispersing agent. Other dispersion tests, including microscopic examination, when compared with dilatancy effects, support the contention that active dilatancy is found only where a most effective dispersion takes place. Therefore

it is believed that dilatancy can be used as a rapid and convenient method of indicating good dispersing agents. This is true only when comparing systems of commensurate particle size, especially microscopic dimensions. Both specific weight and size of the particles have a bearing on the phenomena described above.

Although it is true that actively dilatant systems always exhibit the highest degree of dispersion, it is likewise true that there may still be many agents which will disperse a pigment fairly well without producing an actively or passively dilatant system. The absence of active dilatancy does not necessarily mean that no dispersing effect can be obtained, but rather that a certain very high and stable degree of dispersion cannot be reached.

The same dispersing agent may not be equally effective for all pigments. However it has been found that dispersing agents which produce dilatancy generally have a broader range of applicability than those which do not. Agent A disperses a greater number of different pigments than any other dispersing agent

TABLE IV

0.973 gram chrome yellow (equaling  $\frac{1}{8}$  cc. displacement volume) plus 9.83 cc. aqueous solution in a 10 cc. graduate

	Days of settling				
	1	2	3	4	5
	No. of cc. of sediment				
No Agent .....	9.8	9.4	9.2	9.2	9.2
0.29% Solution (Agent A).....	1.50	1.55	1.56	1.57	1.57
0.29% Solution (Agent C).....	4.10	4.10	4.05	4.02	4.02
0.29% Solution (Agent D).....	5.52	5.52	5.50	5.50	5.50

that the author has tried. However, not all of these pigments have lent themselves to becoming actively dilatant.

#### DILATANCY VS. CONSISTENCY

A discrepancy exists between the dilatancy and sedimentation volume tests on the one hand and the consistency test on the other in the case of agent C. This discrepancy cannot be fully explained as yet, but there is cause to believe that the former tests are more reliable. Agent C has a stronger liquefying effect than agents A and B but produces no dilatancy. At 76% concentration, zinc oxide mixed on a glass plate with a solution of agent A flowed like a viscous oil. When a solution of agent C was used, however, a paste of the same concentration was thin and watery, flowing from a spatula in distinct, single drops.

The difference between the two types of dispersing agent appears even greater when considering the maximum concentration of pigment that can be employed in the production of a homogeneous paste. Owing to the high resistance of dilatant systems to mechanical force, a Banbury mixer was used in the production of these highly concentrated pastes.

Using agent C, a smooth 87.5% zinc oxide paste with a comparatively low yield value was thus made. When thinned with water 1% to 2% below this

concentration, the paste turned into a thin liquid. The most concentrated paste that could be obtained with agent A of the highest possible purity was one containing 86.6% zinc oxide. Above that concentration the mass became dry, crumbly and incoherent. With agent A of technical quality, the highest concentration of zinc oxide obtained was 86.0%.

However, dispersions made from agent C have a paste-like character in only a very narrow range of concentration; they are usually either fluid or dry and lumpy. In the paste state such dispersions do not flow and have a yield value. If a paste of this type is forced against the walls of a containing vessel with a spatula, two separate phases are formed, one consisting of dry lumps and the other of a thin, watery liquid. These lumps do not liquefy when allowed to remain undisturbed, or do they liquefy upon tapping. The dispersion has apparently been destroyed by mechanical forces. On further addition of zinc oxide the entire mixture becomes dry, lumpy, dull and irreversible.

On the other hand a zinc oxide dispersion using agent A, after passing through an extremely fluid stage at low concentrations, enters a range, on increasing the concentration, where it is neither liquid nor dry and lumpy. This range is fairly broad, from 73% to about 86% zinc oxide. In this range the paste is actively dilatant; dry lumps of a lasting nature cannot be formed in one portion while another portion remains fluid. Either the whole system is dry and dull or is smooth and mobile. No two phases can be produced by pressure as in the case of a dispersion with agent C.

As a further distinction between highly concentrated pastes made from agents A and C, pastes containing C offer little resistance to a knife thrust, while those containing A resist such a thrust forcibly, and the whole mass exhibits elastic deformation. In spite of this difference in the character of agent A and C pastes, it is believed that the assumed relation between dilatancy and dispersion generally holds true; *i. e.*, wherever dilatancy exists there must be excellent dispersion.

#### DISPERSION AND PARTICLE ADHESION

The nature of the adhesion forces between particles has been discussed by von Buzagh<sup>7</sup>. The two main factors that determine the degree of adhesion are the  $\zeta$  potential and the thickness and deformability of the solvation layers around the particles. von Buzagh calculates the adhesion forces between particles to be in the neighborhood of 0.3 dynes per sq. cm.; under certain conditions, however, they may become as high as 3 to 6 dynes per sq. cm.

In the case of agent A, only one of the factors involved is known, the  $\zeta$  potential, which can be measured by cataphoresis. It is extremely high, between 65 and 106 millivolts, depending on the degree of purity of the product. Agent B, from which agent A is derived, has a  $\zeta$  potential lower than that of A. This would seem to indicate that the difference in the dilatancy effect produced by the two agents may depend largely on the magnitude of the  $\zeta$  potential. In other words, whatever the role of the solvation layer may be, which is not known in this case, a high  $\zeta$  potential appears to be a main factor in producing actively dilatant systems, *i. e.*, in preventing the attractive or adhesive forces between particles from becoming dominant.

In the case of agent C, the particles appear to keep apart only under favorable conditions, *e. g.*, in dilute systems. The repelling forces do not prove strong enough to keep the particles apart when they are forcibly and closely packed



together, as in the production of highly concentrated pastes. The adhesion forces under these conditions become predominant, and the material will not flow again, even if subjected to vibration. It may be that the character of the liquid medium is changed by C, allowing the solvation layers to become deformed by force to the extent that the particles become associated with each other in a manner similar to the molecules in a solid, but unlike the original loose aggregates which occluded so much water. These original loose aggregates, after being destroyed by the effect of the dispersing agent, give way to a closer packing of the particles. Only after this preliminary packing has taken place does it become possible for outside (mechanical) forces to cause the particles to come so close together that attraction of a higher order of magnitude came into play. This explanation of the behavior of the paste seems entirely possible in the light of von Buzagh's investigation.

In actively dilatant systems, the repelling forces apparently are so strong that a pattern is established, with the particles tending to keep equally distant from each other. If this pattern is upset by outside forces, the resulting effect is only temporary. As soon as the cause of disturbance is removed, the particles under the influence of the strong repelling forces, resume their former equidistant relation; the mass levels out quickly and becomes glossy again<sup>3</sup>. The repelling forces increase as the particles are brought nearer together by impact. The occurring rebound may explain the elasticity found in dilatant systems.

Passively dilatant systems must be assumed to be partly flocculated, or at least to have a less orientated and rigid pattern with weaker repelling forces than in the case of active dilatant systems. The higher amount of water required on mixing a paste, and the fact that excess moisture appears on tapping, bears this out. The thixotropic character of these systems also points to the existence of weak and reversible adhesion forces.

Passive dilatancy and thixotropy are the intermediate steps between complete dispersion and complete flocculation. Where neither active nor passive dilatancy exists and yet highly concentrated pastes can be made, as in the case of agent C, good dispersion may take place only under certain favorable conditions, *e. g.*, in dilute systems.

#### EFFECT OF ELECTROLYTES ON DILATANT SYSTEMS

Whereas mechanical forces fail to change the degree of dispersion of actively dilatant systems, the reduction of the electrokinetic forces below a certain critical value will have an instantaneous destructive effect. The addition of small amounts of electrolytes will change an actively dilatant system to one that is passively dilatant. Larger amounts will bring about complete flocculation. Thus we can reverse step by step the direction on the dispersion scale.

Except for minor deviations from the rule, the *coagulating* effect of electrolytes on hydrophobic sols parallels their ability to decrease the cataphoretic velocity of the dispersed particles. In the same way the influence of the electrolytes on flocculation is governed by the valency rule; trivalent cations such as aluminum are about 10 times as effective as divalent cations such as barium, strontium and calcium (in order of their effectiveness) and about 100 times as effective as monovalent ions such as potassium, sodium and lithium (in order of effectiveness). Free hydrogen ions are even more destructive to dispersions than trivalent cations.



The parallelism between the increase of adhesion between particles and the increase in electrolyte concentration is fairly strict and holds for all dispersions. In general the influence of electrolytes on the dispersion does not result from chemical reactions with the pigment or dispersing agent, but from the effect on the  $\zeta$  potential of the particles and on the solvation layers. This must be kept in mind when working with dispersing agents. No matter how good a dispersing agent may be, the presence of certain salts or acids will effectively counteract its dispersing effect. Electrolytes will also destroy the natural dispersability of a system without dispersing agents.

### SUMMARY

(1) In Part I the difference in the functions of wetting, dispersing and protecting agents is discussed, and explanations of the different mechanisms by which they act are suggested.

(2) The known methods for testing dispersion are cited.

(3) In Part II the dispersing qualities of four different types of agents are compared by the method of sedimentation volume. From the results of this test a newly discovered dispersing agent appears to be the most efficient of the four agents tested.

(4) It is found that this new agent has the peculiar property of making a number of pigments actively dilatant. Dilatancy was previously known only as an inherent property of certain substances, not as a property which can be induced by means of surface active agents.

(5) Dilatancy is linked with dispersion. It is shown that flocculation, thixotropy, passive dilatancy and finally active dilatancy can be regarded as different states of dispersion, with no distinct line of demarcation between them. Active dilatancy is obtained only at a most complete degree of dispersion.

(6) The dilatancy test is regarded as a quick and convenient method of evaluating dispersions in all cases where dispersions of a relatively high degree are obtained.

(7) An inconsistency in the results between the sedimentation volume and dilatancy tests on the one hand and the consistency test on the other hand is discussed. Systems containing agent C show no dilatancy and have a relatively large sedimentation volume; yet they remain fluid at concentrations even higher than those reached by dilatant systems. This discrepancy cannot be fully explained, but it is not believed to invalidate the above deductions on the relation between dilatancy and small volume of sedimentation on the one hand and dispersion on the other hand.

(8) The mechanism of dilatancy is discussed. The  $\zeta$  potential and hydration are assumed to be the most important factors. With the addition of discharging cations, dilatancy is gradually destroyed and the state of dispersion reversed.

### ACKNOWLEDGMENT

The writer is indebted to Prof. H. Freundlich and to E. V. Osberg for their helpful advice and criticism and to Mrs. R. Daniel for providing the experimental data for this article.

## REFERENCES

- <sup>1</sup> After completion of this paper, von Buzagh published a paper on "The Adhesion of Microscopic Particles" (cf. *J. Phys. Chem.* **43**, 1003 (1939)). von Buzagh gives an example illustrating the above statement: gelatin increases the adhesion of quartz particles, yet the stability is improved. However, it must be noted that quartz in water has a particularly low adhesion (0.3 dyne per sq. cm.).
- <sup>2</sup> Freundlich and Jones, *J. Phys. Chem.* **40**, 1217 (1936); Freundlich, *Royal Inst. Great Britain*, Mar. 20, 1936, pp. 1-27.
- <sup>3</sup> Freundlich and Röder, *Trans. Faraday Soc.* **34**, 308 (1938).
- <sup>4</sup> Reynolds, *Phil. Mag.* [5] **20**, 459 (1885); *Nature* **33**, 429 (1886).
- <sup>5</sup> Hauser, "Colloidal Phenomena", McGraw-Hill, New York, 1939, 225.
- <sup>6</sup> Plasticity is another term for what is described in this paper as "paste-like consistency", or as the behavior of a paste having the distinct yield value.
- <sup>7</sup> von Buzagh, *Kolloid-Z.* **51**, 105, 230; **52**, 46 (1930).

# CHLOROFORM EXTRACT OF RECLAIMED RUBBER \*

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The purpose of this paper is to discuss the effects of the processing operations in the manufacture of reclaimed rubber which may affect its solubility in chloroform, and also the significance of the chloroform extract in interpreting the quality and processibility of reclaimed rubber.

The amount of chloroform extract appears to be significant when an examination is made of reclaimed rubber after acetone and chloroform extractions have been made. The residue after extraction is hard and elastic, and on a mill it resembles vulcanized rubber. Obviously, the joint plasticizing action of the extractable plasticizers, which appear chiefly in the acetone extract, and depolymerized rubber, which is the chief component of the chloroform extract<sup>17, 18</sup>, makes possible the production of commercial reclaimed rubber. A number of factors which contribute to the degree of formation of chloroform-extractable material are discussed in this report.

The significance of chloroform extract has been mentioned or discussed by several investigators<sup>8, 7-13, 15-19</sup>. Stafford<sup>16</sup> called attention in 1926 to the presence of the chloroform-soluble portion of reclaimed rubber, and also demonstrated that chloroform-soluble rubber contained a definitely lower proportion of combined sulfur than remained in the chloroform-insoluble portion.

Weber<sup>17</sup> described the chloroform extract, and pointed out the low viscosity of its solution as evidence of a large degree of depolymerization or disaggregation. He pointed out that the amount of chloroform extract did not give an accurate indication of the difference in plasticity between various reclaims.

Winkelmann<sup>18</sup> showed four cases where the chloroform-soluble portion of the reclaimed rubber was from 37 to 45 per cent of the total rubber hydrocarbon of the reclaim, yet this portion contained less than 10 per cent of the combined sulfur. He offered two possible explanations: (a) The chloroform-soluble rubber is rubber that has been merely aggregated in the presence of, but not combined with, sulfur during vulcanization; (b) the chloroform extract consists of fragments of long rubber molecules which have combined with sulfur at one end of the molecule during vulcanization, and which have been broken off during the devulcanization.

Boiry<sup>3</sup> showed that substantially all of the chloroform extract is produced in the early part of the devulcanization period. He showed also that the lower the sulfur content of a reclaim, the greater is its chloroform extract.

Miller<sup>10</sup> showed that repeated vulcanization and reclaiming of rubber results in progressively lower chloroform extracts. These lower values are accompanied by an increasing combined sulfur content of the reclaim. If the high combined sulfur content of the reclaim is considered to be the cause of the low chloroform extract, these results are in agreement with the work of Boiry on the influence of combined sulfur.

Palmer, Miller, and Brothers<sup>13</sup> showed that drying in air at temperatures of 99° to 135° C (210° to 275° F), following digestion in dilute caustic solutions,

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 4, pages 512-518, April 1940.

resulted in an increase of 1.5 to 4 per cent in the chloroform extract over that of reclaim at room temperature.

Zilchert<sup>19</sup> considers that measurement of the chloroform extract is a means of determining the process which has been used in preparing the reclaim, a high extract indicating the use of the alkali process.

Kirchhof<sup>7</sup> expanded Zilchert's thesis by providing data obtained by analysis and testing of some sixteen reclaims, and showed that reclaimed rubbers with high chloroform extracts (30 to 40 per cent of the total rubber) are generally of higher quality than those with lower chloroform extracts. He based his evaluation of quality on the tensile product of the reclaim when vulcanized to its optimum cure with 3 per cent of sulfur and 0.5 per cent of diphenylguanidine. The authors' experience leads them to question the desirability of the use of so simple a test formula, since reclaims which appear poor when vulcanized alone often prove to be perfectly satisfactory when mixed with crude rubber and

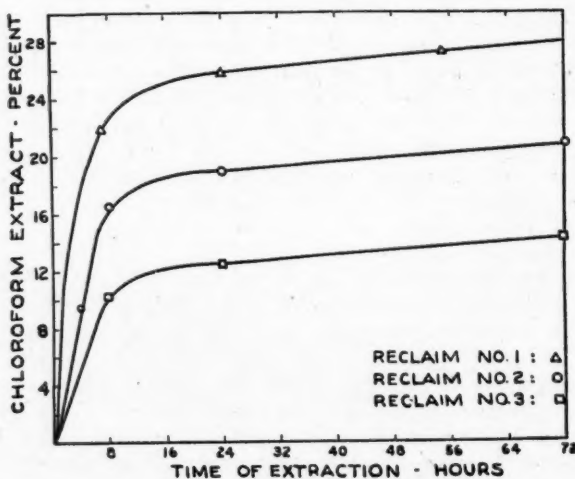


FIG. 1.—Rate of extraction on three different reclaims.

pigments, as usually occurs in practical use of reclaimed rubber<sup>11, 12</sup>. They also prefer to evaluate a reclaim in a test compound on the basis of tensile and elongation separately rather than on tensile product. If one wishes a soft compound after vulcanization, a reclaim with a high elongation will introduce the desired rubbery character. On the other hand, certain applications require a reclaim which will produce a hard or leathery compound. It is felt that for each application there is a reclaim best suited for the purpose, and that the best procedure for evaluating a reclaim is to try it in the recipe for the article that is to be made, finally selecting the reclaim that imparts the desired properties.

From a practical standpoint, for a given reclaim a very low chloroform extract indicates lack of devulcanization, and a high chloroform extract indicates thorough and often excessive devulcanization. It is felt that the chloroform extract of reclaimed rubber is chiefly of theoretical importance because of its analogy to the sol portion of crude rubber, and it is of no practical value in evaluating or interpreting the performance of reclaimed rubber. This report will show what factors in the reclaiming process affect the magnitude of the chloroform extract.

## EXPERIMENTAL PROCEDURE

The methods used for determining acetone extract and chloroform extract are essentially the A. S. T. M. procedures<sup>2</sup> with exceptions as follows:

A 1- or 2-gram sample is prepared by sheeting to a thickness of 0.051 cm.  $\pm 0.005$  (0.020 inch  $\pm 0.002$ ) by passing it through a laboratory mill exactly three times. The mill rolls are heated to a temperature between 38° and 44° C (100° to 111° F). The sample is then weighed on an analytical balance with an accuracy of 0.0005 gram in a single strip about 9×3 cm. (3.5×1 inch). The number of small pieces used to adjust the weight to 1 or 2 grams is kept to a maximum of two. The sample is rolled in the center of a piece of cotton sheeting 10×18 cm. (4×7 inches) in such a way as to confine the sample without hindrance to the swelling action of chloroform. The cotton sheeting is previously extracted with acetone and chloroform. The acetone extraction is run for 16 hours. After draining the acetone from the extraction cup, the chloroform extraction is started immediately, to avoid oxidation of the sample. The chloroform extraction is run for 24 hours. The time of chloroform extraction has been variously suggested from 4 to 72 hours<sup>7, 10, 16-19</sup>. Figure 1 shows the rate of extraction on three different reclaims, and indicates that 8 hours is too short and 72 hours unnecessarily long for this extraction. The amount of chloroform extract removed during the last 48 hours is approximately 2 per cent of the sample. The extract is dried 3 hours at 70° C (158° F) before weighing. The extract is quite stable during drying. Tests have shown that the chloroform extract gains less than 0.1 per cent in weight (based on the sample weight of 1 or 2 grams) when heated for 24 hours at 70° C.

In determining chloroform extract, it is important that the procedure be adhered to rigidly in order that satisfactory check results may be obtained. Results which agree within 1 per cent are acceptable. In acetone extract determinations better agreement is attained. Duplicate determinations should agree within 0.5 per cent.

The chloroform extract of a given reclaim decreases with the age of the reclaim. This should be taken into account in comparing the chloroform extracts of different reclaims. All such comparisons in this paper were made on reclaims of the same age.

The milling test procedure suggested by Palmer, Miller and Brothers<sup>13</sup> was used as a practical means of interpreting plasticity and workability. It consists simply in milling a sample of reclaim on a laboratory-size mill under standardized conditions with respect to batch size, roll temperature, roll speed and roll setting. The times necessary for the reclaim to (a) knit or adhere to the slow roll, (b) reach a definite degree of smoothness or freedom from breaks in the sheet, and (c) leave the slow roll and adhere to the fast roll, provide a numerical record of the behavior of the reclaim. In this work a 40×20 cm. (16×8 inch) mill was used, with a 3 to 2 ratio, 21 and 14 r.p.m. For tire reclaims the roll temperatures at the start of the test were 35° C  $\pm 1.5^\circ$ , the rolls being set with lead wire at an opening of 0.127 cm.  $\pm 0.005$  (0.05 inch  $\pm 0.002$ ). For tube reclaims the mill was set at 0.100 cm.  $\pm 0.005$  (0.039 inch  $\pm 0.002$ ) opening for the first 2 minutes, and then was opened to 0.127 cm.  $\pm 0.005$ . For reclaims with a specific gravity of 1.40 or under, a 1000-gram sample was used, and a 1500-gram sample for higher specific gravities.



## EFFECT OF TIME AND TEMPERATURE OF HEAT TREATMENT

One of the simplest methods of increasing the softness or plasticity of a reclaim is to increase the time or temperature of heat treatment. The effect of such changes on a tube reclaim made by formula 1 are shown in Table I. Formula 1 is as follows:

Passenger No. 2 gray tubes.....	100
Pine tar .....	3
Sodium hydroxide solution (44%)....	3

TABLE I

EFFECT OF TIME AND TEMPERATURE ON INNER-TUBE RECLAIMS TREATED WITH OPEN STEAM

Reclaim	Hours of devulcanization at:				Degree of devulcanization	Acetone ext., %	Chloroform ext., % on 100 of rubber	Milling test, min. to knit to roll
	164.4° C	182.4° C	190.6° C	204.4° C				
A ...	0.5	—	—	—	Very little	8.95	17.00	—
B ...	1.0	—	—	—	Fair	9.35	19.40	8.0+
C ...	3.0	—	—	—	Fair +	8.78	22.65	5.25
D ...	9.0	—	—	—	Fair +	9.05	22.95	4.20
E ...	—	1.0	—	—	Fair +	8.78	28.20	2.20
F ...	—	3.0	—	—	Normal	9.18	31.30	0.90
G ...	—	9.0	—	—	Normal	9.40	30.25	0.60
H ...	—	15.0	—	—	Soft	8.60	31.80	—
I ....	—	—	30.0	—	Very soft	9.80	38.85	—
J ....	—	—	—	2.0*	Excessively soft	10.03	37.82	—
K ....	—	—	—	7.0*	Excessively soft	10.52	39.60	—

\* Plus 1-hour rise period to reach 204.4° C.

These reclaims were devulcanized in open steam. All batches were dried, milled and refined identically.

A decrease in knit time (increase in plasticity) was found as the time or temperature was increased. However, the chloroform extract reached a nearly constant value in the early part of the heating period at each temperature, and thereafter changed but little, in spite of the fact that the reclaim became progressively softer with increased time of treatment. The ultimate chloroform extract increased with each rise in temperature; the values attained at 164.4°, 182.4°, 190.6° and 204.4° C (328°, 359.6°, 375° and 400° F) were 22.95, 31.80, 38.85 and 39.60 per cent, respectively. With increasing severity of the heating treatment, there was a slight increase in acetone extract. This behavior is apparently general, as it has been observed in other experiments in this laboratory.

In another experiment, reclaims were made from giant No. 1 tire peelings in open steam at high pressure in the absence of caustic and oils. The results are given in Table II. The control, L, was made under conditions which produced

TABLE II

EFFECT OF TIME AND TEMPERATURE ON NO. 1 TIRE PEELEINGS TREATED WITH HIGH-PRESSURE STEAM

Reclaim	Devulcanization		Acetone ext. %	Chloroform ext.		Workability
	Time Min.	Temp. °C		%	% on 100 of rubber	
—	Untreated		8.7	4.1	7.3	Not treated
L	8	254	10.70	18.9	33.6	Normal
M	35	263	13.5	29.4	52.3	Very soft
N	120	263	18.8	25.7	45.8	Excessively soft

a reclaim of normal workability. In runs *M* and *N* the time and temperature were high enough to soften the rubber beyond practical limits with respect to processing under ordinary factory conditions. Under these conditions there was also an increase in acetone extract as well as in chloroform extract with increased severity of treatment. In run *N* there appears to have been a transformation of chloroform-extractable material to acetone-extractable material during heating at 263° C (505.4° F).

The preparation of reclaimed rubber at higher temperatures involves shorter periods of devulcanization. Reclaims were made from whole tire scrap in a laboratory digestion apparatus at 192°, 198° and 208° C (378°, 388° and 406° F), using a common formula for all three temperatures. The time of devulcanization was adjusted until the same degree of workability was obtained at each of the three temperatures. The reclaims were analyzed for acetone and chloroform extract, with the results shown in Table III.

The data in Table III show that the devulcanization reaction rate is approximately doubled for each 10° F (5.5° C) rise in temperature. It is also evident that the chloroform extracts of reclaims of equivalent workability are the same in spite of the variation in time and temperature of devulcanization.

TABLE III

VARIATION OF TIME vs. TEMPERATURE OF DEVULCANIZATION OF WHOLE-TIRE RECLAIM TREATED BY THE ALKALI PROCESS

Reclaim	Devulcanization		Acetone ext. (%)	Chloroform ext.		Workability, time in min.		
	Time, hr.*	Temp., ° C (° F)		%	% on 100 of rubber	To knit	To smooth	To go to back roll
O	13	192.2 (378)	11.67	17.15	28.6	0.2	1.30	2.10—
P	6	197.8 (388)	12.32	16.97	28.3	0.2	1.05	2.5 +
Q	2	207.8 (406)	11.55	17.02	28.4	0.2	1.30	2.8
								2.05

\* Does not include 1-hour rise time to reach temperature.

#### EFFECT OF DRYING DEVULCANIZED RUBBER

An investigation of the effect of drying reclaimed rubber in air at various temperatures was mentioned above<sup>13</sup>. This work proved that drying at temperatures of 99° to 135° C (210° to 275° F) increased the chloroform extract 1.5 to 4 per cent over that of reclaim dried at room temperature.

#### EFFECT OF MILLING PROCESS

The next step considered was the milling operation, in which the devulcanized scrap is blended thoroughly, sometimes mixed with pigments and plasticizing agents, and plasticized before refining. For this purpose whole-tire dried scrap was milled for 15 minutes on an 84-inch (2.13-meter) mill at 88-96° C (190-205° F) in one case, and 15 minutes on a mill at 21-27° C (70-81° F) in a second case; in a third case the dried scrap was simply given a loose refining pass to flatten out any large lumps before the actual refining operation. All three reclaims were then refined and strained under identical conditions. Analytical and milling test data are given in Table IV. These show that the milling operation as it is used in the reclaiming process has little effect on the chloroform extract or the workability of the reclaim within the practical range of time and temperature used.

## EFFECT OF STRAINING OPERATION

This operation is an essential one for the purpose of removing nonmagnetic metal from the reclaim, the magnetic metal being largely removed by magnets during grinding of the scrap for devulcanization. The straining operation occurs after the reclaim has received one or more refining passes and before the final or finishing refiner pass. The work necessary to force the reclaim through the fine meshes of the screen results in a considerable elevation of the stock temperature. An attempt was made to strain reclaim at as low and as high temperatures as possible through a 30-mesh screen, wire size 0.014 inch (0.356 mm.), width of opening 0.019 inch (0.49 mm.), 33.5 per cent open area. For this purpose a cold strainer was used in one case with the barrel cooled to 10° C (50° F) with water. In the other case the barrel was heated with steam to 100° C (212° F). The stock temperatures (measured with a Cambridge pyrometer) were much closer together in the two cases than those of the barrel, because even in the cold strainer the severe working of the reclaim raised the

TABLE IV

EFFECT OF MILLING OPERATION ON WORKABILITY AND ANALYSIS OF WHOLE-TIRE RECLAIM

Reclaim .....	<i>R</i>	<i>S</i>	<i>T</i>
Preliminary treatment			
Milling (min.) .....	15	15	None
Mill temp. (° C) .....	88-96	21-27	—
Stock temp. at end of milling period (° C) .....	91-93	57-63	—
Rough refining pass .....	No	No	Yes*
Refining treatment .....	All refined and strained alike		
Analysis %			
Acetone ext. ....	10.80	11.35	11.55
Chloroform ext. ....	20.45	20.70	20.00
Milling test, time in min.			
To knit to front roll .....	1.1	0.9	1.2
To smooth on front roll .....	4.7	5+	5+
To go to back roll .....	5+	5+	5+

\* Temperature of refiner, 71° C.

temperature rapidly. The reclaim used for the straining experiment was a standard, first-grade, alkali, whole-tire reclaim.

There was no difference in the amount of chloroform extract of the hot- and cold-strained reclaims. A comparison of the two reclaims on the mill showed the hot-strained reclaim to be slightly softer and tackier than the cold-strained stock. This difference in the reclaims is apparently too small to show up in the chloroform extract. Data are shown in Table V.

## EFFECT OF REFINER TEMPERATURES AND EXTENT OF REFINING

In the important operation of refining, the dried heat-plasticized scrap is squeezed into a thin sheet between hot rolls (75-120° C or 167-248° F) set closely together (0.0025-0.025 cm. or 0.001-0.010 inch sheet thickness). In view of the high temperature, thinness of the sheet, and large surface exposed, there is ample opportunity for oxidation to occur. It is well known that repeated refining of a reclaim plasticizes it to a large degree. These considerations made it seem likely that the chloroform extract would increase on repeated refining. The experiment was tried first in the laboratory. The mill described above

was set to deliver a relatively heavy sheet, 0.051 cm. (0.02 inch) thick, such as for sheeting a sample for analysis. A sample of whole tire reclaim which had been given two refining passes in the factory was passed through the rolls of the laboratory mill repeatedly. One sample was given two such refinings and another sample ten refinings. Both were then analyzed, with the result that the ten-pass sample showed 22.82 per cent and the two-pass sample showed only 17.15 per cent chloroform extract. The increase in extract of 5.67 per cent may be divided by the number of extra refining passes to show that refining increased the extract by approximately 0.7 per cent per refining pass. It is also clear that the number of refining passes used in preparing a sample for the chloroform extract determination must be rigidly specified to avoid the introduction

TABLE V

EFFECT OF STRAINER TEMPERATURE ON ANALYSIS AND WORKABILITY OF WHOLE-TIRE RECLAIM

Reclaim .....	U	V
First refining .....	Both handled identically	
Straining temp., ° C		
Barrel .....	100	10
Stock .....	126	82
Second refining .....	Both handled identically	
Analysis (percentages)		
Acetone ext. ....	11.60	11.72
Chloroform ext. ....	24.20	24.33
Milling test (time in min.)		
To knit to front roll.....	0.4	0.65
To smooth on front roll.....	2.6	3.3
To go to back roll.....	5.0+	5.0+

TABLE VI

EFFECT OF REPEATED REFINING IN PREPARATION OF SAMPLES FOR ACETONE AND CHLOROFORM EXTRACTION

No. of refining passes at 0.051 cm.	Acetone ext. (%)	Chloroform ext. (%)
2	12.45	17.15
10	12.18	22.82

of error during analysis. To the knowledge of the writers, this possibility has not been pointed out previously. There was no significant change in the amount of the acetone extract which accompanied the chloroform extraction in the above experiment. The data are given in Table VI.

Whole-tire reclaim was then refined repeatedly in the laboratory and factory, the same lot of scrap being used for both experiments. The factory refining was performed on a standard refiner, 91.5 cm. (36-inch) roll length, having a 3 to 1 speed ratio of fast and slow rolls. The fast roll had a diameter of 61 cm. (24 inches), the slow roll, 51 cm. (20 inches).

Approximately 200 pounds (90 kg.) of strained stock were refined into slabs, the last portion of stock in the refiner (tailings) being rejected. After a sample had been saved, the finished material was returned to the refiner and refined again. This operation was repeated until samples having six refining passes had been obtained. The same lot of strained stock was also refined and again

refined in the laboratory on the laboratory refiner previously described. Roll temperatures were measured, and an attempt was made to keep them as close as possible in factory and laboratory parts of this experiment. The average roll temperatures were 6° C lower in the factory than in the laboratory. As shown later in this report, small differences in refiner temperature do not affect the chloroform extract.

TABLE VII

## EFFECT OF REPEATED REFINING ON ANALYSIS AND WORKABILITY OF WHOLE-TIRE RECLAIM

(All scrap given first refining and straining under identical conditions in the factory)

	Factory	Laboratory
Av. temp. slow roll (° C).....	52-60	71-74
Av. temp. fast roll (° C).....	66-82	71-74
Av. sheet thickness (cm.).....	0.016	0.015
Analysis and milling test (2 refinings)		
Reclaim .....	W-A	W-C <sup>a</sup>
Acetone ext. (%).....	10.72	10.67
Chloroform ext. (%).....	20.53	18.52
Time to knit (min.).....	0.6	—
Time to smooth (min.).....	2.5	—
Time to back roll (min.).....	5.0+	—
Six refinings		
Reclaim .....	W-B	W-D <sup>b</sup>
Acetone ext. (%).....	10.70	10.75
Chloroform ext. (%).....	25.07	21.27
Time to knit (min.).....	0.2	0.3
Time to smooth (min.).....	1.0	1.6
Time to back roll (min.).....	1.3	1.9

<sup>a</sup> Second refining in laboratory.

<sup>b</sup> Five refinings in laboratory.

TABLE VIII

## EFFECT OF RE-REFINING A RED BUS-TUBE RECLAIM

Reclaim .....	X-A	X-B	X-C	X-D	X-E
No. of refining passes.....	3	4	5	6	7
Acetone ext. (%).....	8.40	8.25	—	—	8.57
Chloroform ext. (%).....	17.12	17.35	—	—	19.72
Milling test (time in min.)					
To knit .....	0.8	0.65	0.7	0.5	0.4
To smooth .....	3.1	2.6	2.5	1.7	1.4
To back roll.....	5.0+	5.0+	5.0+	5.0+	5.0+

The data in Table VII show clearly that repeated refining increases chloroform extract. The increase in the factory experiment amounted to 4.54 per cent for four extra refining passes, and the corresponding increase for laboratory refined stock was 2.75 per cent. These amount to 1.13 and 0.69 per cent per refining pass, the latter figure being in agreement with that found in the first refining experiment.

A similar increase has been obtained on repeated refining of a red tube reclaim in the factory. In this case the increase amounted to 0.65 per cent per refining. These data are given in Table VIII. Milling tests in both Tables VII



TABLE IX  
EFFECT OF HOT vs. COLD REFINING TEMPERATURES ON WHOLE-TIRE RECLAIMS

Reclaim	Roll	Slow-roll temp. (° C)	Fast-roll temp. (° C)	Stock temp. (° C)		Strainer	Acetone ext. (%)	Chloroform ext. (%)	Milling test, min. to:		
				1st refiner	2nd refiner				Knit	Smooth	Back roll
Y-A	Cold	75	92	68		108	10.93	21.15	0.5	4.5	5.0+
Y-B	Hot	103	99	76		113	10.72	21.13	0.6	4.0	5.0+
Y-C	Cold	68	86	67		NS*	12.25	17.85	0.7	7.3	5.0+
Y-D	Hot	96	116	72		NS	12.40	17.95	0.9	7.0	5.0+
Y-E	Cold	77	82	68	71	NS	11.75	21.05	0.7	4.1	5.0+
Y-F	Hot	138	138	93	96	NS	12.12	19.42	0.6	4.0	5.0+
Y-G	Cold	49	63	60	49	NS	11.60	25.77	0.5	3.8	5.0+
Y-H	Hot	132	118	102	79	NS	11.58	23.72	0.6	4.2	5.0+

\* Not strained.

and VIII show that repeated refining plasticizes and softens the reclaim. As pointed out above, this behavior is well known.

The effect of the temperature of the refiner rolls on the amount of chloroform extract was investigated by refining at low and high temperatures, the experiment being repeated a number of times. These trials are summarized in Table IX. The conclusion drawn from these tests is that the difference in the effect of hot and cold refining rolls on the stock is too small to show up in chloroform extract or milling tests unless the rolls differ in temperature by at least 50° C. This is probably due to the fact that the scrap comes in actual contact with the hot rolls for only a short period of time, so that the changes which occur during refining are not greatly affected by the roll temperature, at least up to temperatures in the range 50° to 150° C (122° to 302° F). When there is sufficient difference in the temperature of the refiners as in the last two parts of Table IX, a difference in the chloroform extract appears. The reclaim which has been refined on the colder refiners has the higher chloroform extract. These observations are in accord with those of Busse<sup>4</sup> and Busse and Cunningham<sup>5</sup> regarding oxidation and cold milling of crude rubber. The effect

TABLE X

EFFECT OF HOT *vs.* COLD PILING OF WHOLE-TIRE RECLAIM ON WORKABILITY AND CHLOROFORM EXTRACT

Reclaim	Piling treatment	Acetone ext. (%)	Chloroform ext. (%)	Workability, min. to:		
				Knit	Smooth	Back roll
Z-A.....	Cold (30° C).....	12.20	25.13	0.4	3.0	5.0+
Z-B.....	68.3° C .....	12.00	25.80	0.75	5.7	6.0+
Z-C.....	Cold, then heated 25 hr. at 100° C.....	12.75	25.97	1.2	6.5	8.0+

of refining is to increase chloroform extract, and the more severe working which the reclaim undergoes on a cold refiner results in a greater increase in the extract. There was little difference in the workability of the finished reclaims.

#### EFFECT OF COOLING AFTER REFINING OR HEATING DURING STORAGE

Reclaimed rubber is produced in slabs 1 to 3 cm. thick which are generally piled one on top of the other as they are taken from the finishing refiners. Consequently the material cools rather slowly, and work was conducted to show the effect of slow *vs.* rapid cooling on workability and chloroform extract. From one run of reclaim, slabs were produced 1.6 cm. (0.6 inch) thick, some of which were cooled on metal trays individually and others were stored while hot in a pile about 3 feet high (91 cm.). The temperature of the reclaim was measured by means of thermocouples placed in the center of the slabs. The slabs cooled individually came down from the original temperature of 68.5° C (155° F) to a room temperature of 30° C (86° F) in 1.5 hours, whereas the slabs in the center of the pile stayed close to the original temperature of 68.5° C for approximately 8 hours before starting to cool appreciably, and required 6 days to cool down to room temperature. For a further check a slab of the rapidly cooled reclaim was reheated 25 hours at 100° C (212° F) and then examined with the other two samples. These results (Table X) show that the chloroform extract was unaffected either by heating in the pile or by reheating after cooling. As judged by the milling test, the reclaim which was piled hot and also the reclaim which was reheated were definitely less tacky and nervier, since they

required a longer time to smooth and knit to the rolls. Apparently heating after refining promotes a stiffening of the reclaim or a change in processibility without significant effect on the chloroform extract.

#### EFFECT OF AGING RECLAIM

The tendency of reclaimed rubber to become drier and more nervy during natural aging was measured by running chloroform extracts on two whole-tire reclaims over a period of several weeks. These extracts show a distinct decrease as the age of the reclaim increases (Table XI). There is a concurrent drying and nerving of the reclaim when it is milled.

Experience has shown that the nerving process is accelerated by heat. The change may be similar to that which occurs in the natural aging of crude rubber after milling. This has been discussed by Carson<sup>6</sup>. A possible explanation of the aging phenomenon would be the occurrence of a delayed process of vulcanization or repolymerization, probably involving oxygen in the reaction.

TABLE XI

EFFECT OF AGE OF RECLAIM ON CHLOROFORM EXTRACT OF WHOLE-TIRE RECLAIMS

Reclaim	Age when tested (days)	Acetone ext. (%)	Chloroform ext. (%)
Z-D .....	7	10.72	20.53
	60	10.90	16.05
	98	10.77	14.85
Z-E .....	0	8.05	21.20
	7	8.90	19.82
	14	8.15	19.50
	28	9.25	18.17

Another possibility is that the harder or gel phase of reclaimed rubber tends to swell in, or absorb, the soft soluble phase, analogous to the absorption of water by glue, resulting in a harder and drier reclaim.

#### EFFECT OF TYPE OF SCRAP

The variation in resistance to heat treatment of various types of scrap rubber is well known to every reclaimed rubber manufacturer. It is usually attributed to differences in composition, age and degree of weathering, or oxidation. To illustrate the differences between various scraps, six commercial varieties were plasticized side by side in open steam for 9 hours at 182° C (360° F), using Formula 2:

Scrap (chopped to pass $\frac{1}{4}$ -inch screen).....	100
Sodium hydroxide (44%).....	2
Solvenol No. 3 (boiling range 169-198° C or 336-388° F)...	2
Heavy asphalt .....	2

After the heat treatment, each scrap was massed on the mill and given three refinings to produce a sheet 0.013 cm. (0.005 inch) in thickness. Complete analytical data are shown in Table XII. The rubber contents given were calculated by the standard difference method<sup>1</sup>. The degree of plasticization was judged by observing the smoothness, softness, stretch and tackiness of the reclaim as it was being refined. The solid tire and No. 1 peelings scraps were so difficult to soften that the individual leaves of refined reclaim would not cohere

TABLE XII  
EFFECT OF TYPE OF SCRAP ON CHLOROFORM EXTRACT

Reclaim	Type of scrap	Plasticization	Acetone ext. (%)	Chloroform ext. (%)	Ash (%)	Carbon black (%)	Total sulfur (%)	Rubber content (%)	Chloroform ext. (% on 100 of rubber)
A-A	Solid tire	Very little	5.90	5.92	34.62	13.40	2.39	43.7	13.5
A-B	No. 1 giant peelings	Little	10.57	9.08	11.65	21.35	2.09	54.3	10.8
A-C	Bus tubes (red)	Fair	8.25	12.25	30.23	—	1.86	59.7	20.5
A-D	Bus tubes (black)	Fair	8.98	15.90	13.07	17.80	1.96	58.2	27.4
A-E	No. 2 passenger tubes (black)	Good	7.32	26.00	13.25	9.80	2.27	67.4	38.6
A-F	No. 2 passenger tubes (gray)	Quite soft	9.34	21.92	19.75	0.57	2.54	67.8	32.4

to form a solid slab during the last refining. The red and black bus-tube reclaims were more thoroughly plasticized, and the two passenger tube reclaims were similar to commercial reclaims. The chloroform extracts follow the same order as the degree of devulcanization. Table XII shows that reclaims with less than 20 per cent of chloroform extract, based on the rubber content, are insufficiently plasticized; those with 20 to 30 per cent of chloroform extract are reasonably well plasticized; those with greater than 30 per cent correspond to commercial reclaims in workability. However, it is also evident from the data in Tables I and II that the chloroform extract is an insensitive criterion of workability.

The effect of the composition of the scrap is clearly indicated in this series of tests. Solid tires are compounded to be particularly heat resistant through the use of a high zinc oxide content and a high sulfur content. The treads or peelings are tough on account of high carbon black content, and bus tubes are characterized by heat-resistant antioxidants and accelerators.

TABLE XIII

## CHLOROFORM EXTRACTS OF TYPICAL COMMERCIAL RECLAIMS

Reclaim	Type of reclaim	Sp. gr.	Chloroform ext. (% on 100 of rubber)
A-G	Alkali whole-tire reclaim No. 1	1.13	44
A-H	Alkali whole-tire reclaim No. 2	1.15	40
A-I	Second-grade tire reclaim	1.18	37
A-J	Red passenger-tube reclaim No. 1	1.19	34
A-K	Red passenger-tube reclaim No. 2	1.20	33
A-L	Neutral No. 1 peelings reclaim	1.15	32
A-M	Red bus-tube reclaim	1.28	30
A-N	Black blend reclaim	1.36	28

## TYPICAL COMMERCIAL RECLAIMS

Table XIII gives the values of the chloroform extract for typical commercial reclaims based on the rubber content, determined by the standard difference method<sup>1</sup>. The lowest value is 28 per cent for a medium-gravity, black blend reclaim, which undoubtedly contains considerable re-reclaimed rubber<sup>10</sup>, and the highest is 44 per cent for a first-grade whole-tire reclaim.

## VALUE OF ACETONE-EXTRACTABLE VS. CHLOROFORM-EXTRACTABLE PORTION OF RECLAIMED RUBBER

In the introduction it was pointed out that the joint plasticizing action of oils and depolymerized rubber makes possible the utilization of reclaimed rubber. It is possible to show that reclaimed rubber of substantially equal quality can be made by either of two methods as follows: a moderate heat treatment with addition of a large quantity of oils, A-O; a severe heat treatment with no addition of oils, A-P.

The addition of oils in method A-O was made so that the total extract, acetone and chloroform was approximately the same for both reclaims. Formulas and analyses for the two reclaims are shown in Table XIV.

The similarity of the two reclaims from a workability standpoint was judged by their behavior on the mill and by the way in which they took up pigment on the mill in a standardized loading test<sup>11</sup>. Reclaim A-O took up a maximum



load of 300 per cent of whiting based on the reclaim; *A-P* took up 325 per cent under the same conditions. The rates of incorporation of the pigment were 21 and 23 per cent per minute, respectively, and these figures indicate further the similar character of the reclaims.

As a test of the equivalence of reclaims *A-O* and *A-P*, they were compared in the following typical tire friction test formula (No. 3):

Smoked sheet .....	31.62
Reclaim .....	50.00
Zinc oxide .....	1.25
Sulfur .....	2.00
Mercaptobenzothiazole .....	0.38
Stearic acid .....	0.75
Pine tar .....	2.00
Whiting .....	12.00
Total .....	100.00

TABLE XIV

## RECLAIMS WITH HIGH ACETONE AND HIGH CHLOROFORM EXTRACTS

Reclaim .....	<i>A-O</i>	<i>A-P</i>
Devulcanization formula		
No. 2 gray tubes (hogged) .....	100.0	100.0
Heavy pine tar .....	3.0	3.0
Sodium hydroxide .....	1.3	1.3
Hours in open steam		
164.4° C (328° F) .....	3.0	—
190.6° C (375° F) .....	—	30.0
Mill room formula		
Devulcanized scrap .....	88.51	100.00
Heavy paraflux .....	3.83	—
Pine tar .....	3.83	—
Medium-process oil .....	3.83	—
Total .....	100.00	100.00
Mixing and refining .....	Same for both reclaims	
Acetone ext. (%) .....	18.10	9.80
Chloroform ext. (%) .....	18.80	26.00
Total (%) .....	36.90	35.80

Slabs of this compound were cured and tested. The results (Table XV) proved that *A-O* was the better reclaim with respect to tensile strength. Similar results were obtained in a low-grade mat formula. It is unnecessary to give these data here, since the above comparison is an exaggerated one. This was intentional in order to prove that, contrary to popular opinion among rubber technologists, the reclaimer is able to use oils as plasticizers in preference to more thorough heat plasticization without seriously degrading the product. In many applications of reclaimed rubber, it is preferable to retain as much of the original strength of the rubber as possible by limiting the heat treatment, at the same time providing the necessary concentration of plasticizing agents in the form of added oils. In other applications where inertness, smoothness, and complete freedom from partly devulcanized lumps are essential, it is necessary to carry the heat treatment much further. As pointed out previously<sup>11, 12</sup>, final judgment on a reclaim should be made only when it is tested for performance in the compound for which it is intended.

## DISCUSSION OF RESULTS

This paper throws little light on the origin of the chloroform-extractable portion of reclaimed rubber. It undoubtedly originates from a thermal cracking of the vulcanized rubber complex in greater or lesser amounts, depending on the history of the scrap, on the temperature of the devulcanization process, and to a limited extent on the time of the devulcanization process. Other factors such as drying temperature<sup>9</sup> and degree of severity of refining also affect the magnitude of the chloroform extract.

From a theoretical standpoint the solution of the problem of the thermal breakdown of vulcanized rubber must probably await the explanation of vulcanization itself. The problem is complicated by the presence of combined oxygen as a natural constituent of vulcanized scrap rubber. The reclaiming process from grinding to refining, since it is conducted in the presence of air, must be dependent on the chemical and catalytic action of oxygen to a considerable extent<sup>4, 5, 14</sup>.

TABLE XV.

RECLAIMS WITH HIGH ACETONE AND HIGH CHLOROFORM EXTRACTS IN A RECLAIM FRICTION COMPOUND

Reclaim .....	A-O	A-P
Cure 15 min. at 126.9° C		
Stress at 300% elongation (kg. per sq. cm.).....	16.5	16.2
Elongation (%) .....	765	750
Tensile strength (kg. per sq. cm.).....	148.0	118.0
Cure 30 min. at 126.9° C		
Stress at 300% elongation (kg. per sq. cm.).....	26.0	26.0
Elongation (%) .....	685	700
Tensile strength (kg. per sq. cm.).....	156.0	138.8
Cure 45 min. at 126.9° C		
Stress at 300% elongation (kg. per sq. cm.).....	29.9	25.0
Elongation (%) .....	660	655
Tensile strength (kg. per sq. cm.).....	155.6	134.2

The measurement of the chloroform extract is not a practical method of determining the degree of devulcanization of reclaimed rubber. This may be readily seen if one compares reclaims on the mill which have been prepared with short and long periods of devulcanization, such as are illustrated in Table I. The chloroform extracts may be relatively close together, yet the reclaim with the shorter cook will be decidedly dry and nervy on the mill whereas the other is tacky and inert. It is apparent that the chloroform extract is not the only factor affecting workability. Possibly a method of examining the chloroform-insoluble portion as well as the chloroform-soluble part of reclaimed rubber would provide a more accurate analytical method for evaluating reclaimed rubber. Such a method would be of value to reclaimers and reclaim users alike. Until a better method of chemical examination is evolved, the milling test and use of test formulas will continue to be standard procedures for evaluating reclaimed rubber.

## CONCLUSIONS

1. For any given reclaim, increased chloroform extract means greater softness and plasticity, but different types of reclaim with equivalent chloroform extracts may have widely different plasticities, or with the same workability may have widely different chloroform extracts.

2. While longer time of heat treatment at a given temperature increases the chloroform extract, increased temperature raises it decidedly. At elevated temperature (263° C) there is a transformation of chloroform-soluble into acetone-soluble material.

3. Within practical operating temperature limits, the milling and straining operations do not affect the chloroform extract. Increased number of passes through a refiner increases the chloroform extract. This fact is of importance in the chloroform determination. Cool refining gives a product with higher chloroform extract than hot refining.

4. The chloroform extract is unaffected by slow or rapid cooling of finished reclaim slabs. The slow-cooled reclaim, however, is somewhat drier and nervier.

5. Reclaimed rubber has a lower chloroform extract after natural aging than when freshly made. The aging process is also accompanied by an increase in the nerve and a decrease in the tackiness of the reclaim.

6. The use of oils as plasticizers in preference to excessive heat plasticization is not detrimental to reclaim quality, but is often desirable in producing many types of reclaimed rubber.

7. The percentage of chloroform extract present in typical commercial reclaims usually lies between 30 and 40 per cent, based on the rubber content. Values below 20 per cent indicate a low degree of devulcanization. Values above 50 per cent are rare but, when they do occur, indicate an excessive devulcanization. The amount of chloroform extract is an insensitive criterion of workability. Since a high chloroform extract does not indicate improved quality, a performance test must be used.

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# REFRACTOMETER STUDIES ON RUBBER-PIGMENT MIXTURES \*

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Several years ago, McPherson and Cummings<sup>3</sup> published data on the refractive index of rubber and of rubber-pigment mixtures. They found no difference in the refractive index of rubber from various sources. The degree of mastication did not appreciably change the refractive index. Sulfur in combination with rubber altered the refractive index relatively more than free sulfur in rubber. With the exception of zinc oxide, the pigments and fillers they examined did not affect the refractive index. In the case of zinc oxide, there was a significant increase in refractive index and the fine particle size oxide (Kadox) developed a higher value than the coarser oxide (XX Red). They suggested that zinc oxide probably reacts with the nonrubber components to form salts which dissolve and change the refractive index.

This laboratory<sup>5</sup> found that, for a series of various particle size zinc oxides in rubber, the increase in refractive index was inversely proportional to the particle size of the oxides; that is, a fine particle size zinc oxide increased the refractive index somewhat more than a coarse oxide. It was also observed that the refractive index of zinc oxide-rubber mixtures increased proportionally with each addition of zinc oxide until the opacity of the zinc oxide-rubber mixture became too great (over 6 per cent) to allow measurement by transmitted light.

## EFFECT OF PIGMENTS ON REFRACTIVE INDEX

The present investigation was undertaken to extend the work of McPherson and Cummings and gain some understanding of the effect of zinc oxide and other pigments on refractive index. The refractive index measurements were made with an Abbé refractometer, with a carbon arc as a source of illumination. Small samples (5 to 10 grams) of the rubber stocks were squeezed into thin films between layers of metal foil in a cold press, and the rubber films were mounted in the refractometer for determinations by transmitted light.

To determine whether the increase in refractive index of zinc oxide-rubber mixtures is due to a reaction between zinc oxide and the nonrubber components of crude rubber, samples of acetone-extracted rubber, deproteinized rubber and purified rubber hydrocarbon were compounded with Kadox zinc oxide (0.12 micron), and measurements were made on the Abbé refractometer. The refractive indices (Table I and Figure 1) of the several rubbers were substantially the same at equal concentrations of zinc oxide, which indicates that the phenomenon is not due to a reaction of zinc oxide with the nonrubber components of the crude rubber. This is further indicated by the fact that the refractive index of other rubberlike materials, such as Neoprene and Perbunan, shows an increase in refractive index when increments of zinc oxide (Table II) are added to them, and the magnitude of the change of refractive index is of the same order as with natural rubber.

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 32, No. 3, pages 331-334, March 1940.

The influence of mastication on the refractive index was studied by incorporating zinc oxide in latex and making measurements on dipped latex films containing 0, 0.5, 1.0, 2.0 and 4.0 per cent zinc oxide. To ensure good dis-

TABLE I  
REFRACTIVE INDEX ( $n_D^{25}$ ) OF NATURAL RUBBER AND SEVERAL MODIFICATIONS OF NATURAL RUBBER

	Pale crepe	Acetone-extd. pale crepe	Deproteinized rubber	Pure rubber hydrocarbon
Rubber .....	1.5192	1.5190	1.5194	1.5194
Rubber + 0.5% ZnO (0.12 micron) .....	1.5202	—	1.5202	1.5200
Rubber + 1.0% ZnO ...	1.5206	—	1.5206	1.5205
Rubber + 2.0% ZnO ...	1.5212	1.5215	1.5211	1.5211
Rubber + 3.0% ZnO ...	1.5222	—	1.5220	—
Rubber + 4.0% ZnO ...	1.5228	1.5230	1.5228	—
Rubber + 6.0% ZnO ...	1.5240	1.5242	1.5236	1.5240

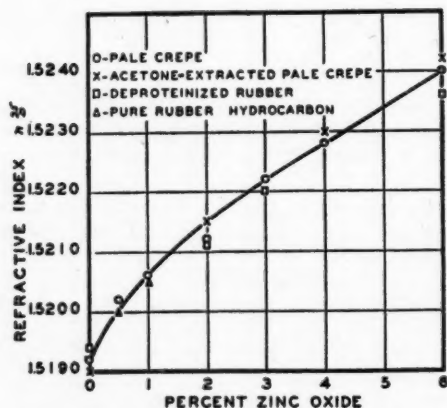


FIG. 1.—Refractive index of natural rubber and several modifications of natural rubber.

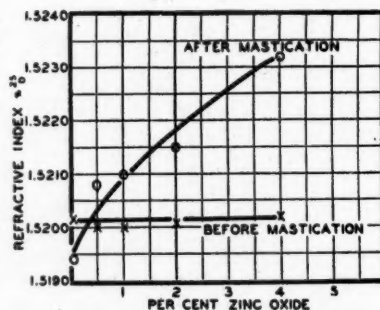


FIG. 2.—Refractive index measurements on latex-zinc oxide mixes.

TABLE II  
REFRACTIVE INDEX MEASUREMENTS ON SYNTHETIC MATERIALS

	Neoprene		Perbunan		Pale crepe	
	$n_D^{25}$	$n_D^{30}$	$n_D^{25}$	$n_D^{30}$	$n_D^{25}$	$n_D^{30}$
Blank .....	1.5580	1.5562	1.5213	1.5198	1.5192	1.5174
0.5% ZnO (0.12 micron) .	1.5580	1.5560	1.5231	1.5216	1.5202	1.5184
1.0% ZnO .....	1.5585	1.5562	1.5242	1.5225	1.5206	1.5189
2.0% ZnO .....	1.5592	1.5570	1.5240	1.5220	1.5212	1.5194
3.0% ZnO .....	—	—	1.5251	1.5231	1.5220	1.5200
4.0% ZnO .....	1.5602	1.5582	1.5260	1.5244	1.5228	1.5209
6.0% ZnO .....	1.5610	1.5560	1.5262	1.5248	1.5240	1.5221

persion, the zinc oxide was ball-milled for 16 hours with casein and Darvan (a commercial wetting agent) in water, and this suspension was stirred into a 60 per cent latex emulsion. The films, irrespective of zinc oxide content, had the same refractive index (Table III and Figure 2), and were essentially equal



to unpigmented rubber. However, when the films were masticated on a 6-inch laboratory mill, the compounds containing zinc oxide were found to have higher values, and the measurements were in close agreement with those for pale crepe-zinc oxide mixtures (Table I).

The increase in refractive index, therefore, is associated with mastication, although it occurs only when zinc oxide is present. Parallel experiments were made by incorporating zinc oxide in a rubber cement (Table IV), evaporating the solvent, and measuring the refractive index before and after milling of the dried cement film; again an increase in refractive index was noted after milling. In this instance somewhat lower values were observed for the films

TABLE III  
REFRACTIVE INDEX MEASUREMENTS ON LATEX-ZINC OXIDE MIXES<sup>a</sup>

	$n_D^{25}$	$n_D^{30}$
Dipped films		
Latex film .....	1.5200	1.5182
Latex + Darvan + casein .....	1.5202	1.5181
Latex + Darvan + casein + 0.5% ZnO <sup>b</sup> .....	1.5200	1.5190
Latex + Darvan + casein + 1.0% ZnO .....	1.5200	1.5190
Latex + Darvan + casein + 2.0% ZnO .....	1.5201	1.5190
Latex + Darvan + casein + 4.0% ZnO .....	1.5202	1.5191
Dried films masticated on the mill		
Latex + Darvan + casein .....	1.5194	1.5172
Latex + Darvan + casein + 0.5% ZnO <sup>b</sup> .....	1.5208	1.5185
Latex + Darvan + casein + 1.0% ZnO .....	1.5210	1.5188
Latex + Darvan + casein + 2.0% ZnO .....	1.5215	1.5194
Latex + Darvan + casein + 4.0% ZnO .....	1.5232	1.5211

<sup>a</sup> Preparation: 200 grams zinc oxide, 4 grams Darvan No. 1, 10 grams casein solution (20 per cent), and 200 grams water ball-milled 24 hours. Slurry added to 60 per cent latex.

<sup>b</sup> 0.12 micron.

TABLE IV  
REFRACTIVE INDEX MEASUREMENTS ON RUBBER CEMENTS

	$n_D^{25}$
Rubber cement	
Film after 1 hr. in vacuum oven at 50° C. ....	1.5190
+ 4% ZnO after 1 hr. in vacuum oven at 50° C. ....	1.5142
+ 4% ZnO after 1 hr. in vacuum oven at 50° C, milled. ....	1.5162

recovered from the zinc oxide cements, probably because some of the organic solvent adsorbed on the surface of the zinc oxide was not released during the drying of the cement film and resulted in a lowering of the refractive index.

Menadue<sup>4</sup> demonstrated that zinc oxide could be completely dissolved from an uncured rubber-zinc oxide stock by treatment with an ether-acetic acid solution. This suggested the possibility of measuring the refractive index of a rubber film after the zinc oxide had been removed. The rubber-zinc oxide films were immersed in a 20 per cent acetic acid-80 per cent ether solution for 10 days. Then the films were extracted with hot acetone in a Soxhlet extractor and dried in a vacuum desiccator. Refractive index measurements were taken immediately after the evaporation of the acetone. The data in Table V show that the extraction of zinc oxide from the rubber-zinc oxide compounds lowered the refractive index to approximately that of unpigmented rubber.

When stearic acid was added to the series of zinc oxide compounds, the refractive indices of the stocks were lowered, and 10 per cent stearic acid was somewhat more effective than 3 per cent stearic acid (Table VI and Figure 3). The addition of 2, 4 and 6 per cent zinc stearate to rubber did not appreciably change the refractive index of rubber. Examination of the data in Figure 3

TABLE V

EFFECT OF EXTRACTION ON REFRACTIVE INDEX OF ZINC OXIDE FROM PALE CREPE-ZINC OXIDE FILMS

	Before extn.		After extn.	
	$n_D^{25}$	$n_D^{30}$	$n_D^{25}$	$n_D^{30}$
Rubber .....	1.5190	1.5172	1.5192	1.5172
Rubber + 2.0% ZnO (0.12 micron) .....	1.5210	1.5190	1.5202	1.5180
Rubber + 4.0% ZnO .....	1.5231	1.5210	1.5202	1.5180
Rubber + 6.0% ZnO .....	1.5240	1.5221	1.5200	1.5180

TABLE VI

EFFECT OF STEARIC ACID ON REFRACTIVE INDEX OF ZINC OXIDE-RUBBER MIXTURES ( $n_D^{25}$ )

	With- out stearic acid	With 3% stearic acid	With 10% stearic acid	Measurements on rubber-Zn stearate mixtures without ZnO
Pale crepe control....	1.5190	1.5192	1.5180	Pale crepe control 1.5190
0.5% ZnO				
(0.12 micron) .....	1.5202	1.5195	1.5190	
1.0% ZnO .....	1.5206	1.5195	1.5192	
2.0% ZnO .....	1.5212	1.5202	1.5200	2% Zn stearate.. 1.5190
3.0% ZnO .....	1.5220	—	—	
4.0% ZnO .....	1.5230	1.5220	1.5210	4% Zn stearate.. 1.5200
6.0% ZnO .....	1.5240	1.5221	1.5210	6% Zn stearate.. 1.5200

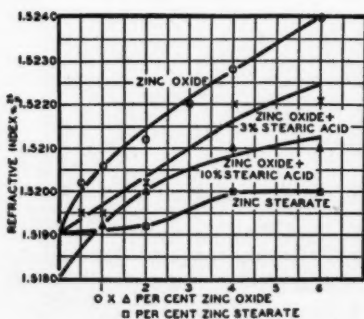


FIG. 3.—Effect of stearic acid on the refractive index of zinc oxide-rubber mixtures.

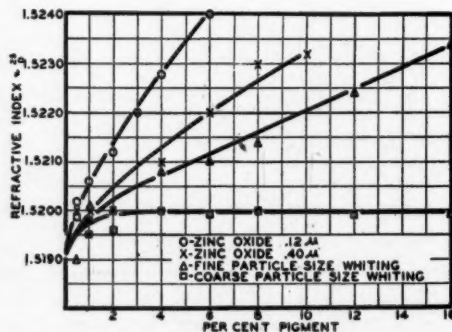


FIG. 4.—Refractive index measurements on zinc oxides and whittings of several particle sizes.

indicates some solution of zinc oxide in the stocks containing stearic acid. For example, the compound with 3 per cent zinc oxide and no added stearic acid had the same refractive index value as the 4 per cent zinc oxide compound with 3 per cent stearic acid; this suggests that 1 per cent of zinc oxide was dissolved by the stearic acid. Similarly in the series of stocks with 10 per cent stearic acid, the 4 per cent zinc oxide compound had the same refractive index as the 2 per cent zinc oxide stock containing no added stearic acid. In this case it appears that 2 per cent zinc oxide was dissolved by the stearic acid.

The zinc stearate formed by the reaction probably did not affect the refractive index, as shown by the group of zinc stearate compounds.

Other pigments and fillers were examined, but the most notable results were obtained with a sample of extremely fine particle size precipitated whiting, which increased the refractive index of rubber to a considerable extent. The curves in Figure 4 illustrate the values obtained for the precipitated whiting compared with a natural whiting (finely ground) and zinc oxides of different particle size. The low opacity of whiting permitted the measurement by transmitted light of higher concentrations of this material. From these curves it can be concluded that the observed refractive index changes are closely associated with the particle size of the pigments (Table VII).

Additions of 4 per cent of lead, cadmium and calcium oxides increase the refractive index from 1.5190 to approximately 1.5200, which is about 25 per cent of the increase noted for the same amount of zinc oxide (0.12 micron). Because of the high opacity of titanium oxide and zinc sulfide, only 2 per cent additions could be measured, and these showed an increase from 1.5190 to 1.5200.

TABLE VII

REFRACTIVE INDEX MEASUREMENTS ( $n_D^{25}$ ) ON ZINC OXIDES AND WHITINGS OF SEVERAL PARTICLE SIZES

Parts of pigment or inert/100 parts rubber	Zinc oxide			Whiting	
	0.12 micron	0.40 micron	1.0 micron	Precipi- tated	Finely ground
Pale crepe control.....	1.5190	1.5189	1.5189	1.5190	1.5190
0.5 .....	1.5202	1.5200	1.5200	1.5190	1.5198
1.0 .....	1.5206	1.5200	1.5200	1.5201	1.5195
2.0 .....	1.5212	1.5210	1.5200	1.5200	1.5196
4.0 .....	1.5228	1.5220	1.5199	1.5208	1.5200
6.0 .....	1.5240	1.5230	1.5198	1.5208	1.5198
8.0 .....	—	—	—	1.5214	1.5200
12.0 .....	—	—	—	1.5224	1.5199
16.0 .....	—	—	—	1.5234	1.5199

Since samples of various particle sizes were not available, it is impossible to predict whether these pigments have a coarse effective particle size or whether they do not cause the same change in refractive index as does zinc oxide and whiting. The author's opinion is that the latter is true in the case of zinc sulfide and titanium oxide. The opacity of carbon black permitted the incorporation of only 0.1 per cent, and this amount of soft carbon increased the refractive index from 1.5190 to 1.5200. Channel black gave the surprising value of 1.5050 with a 0.1 per cent addition, and this was believed to be due to the adsorbed hydrocarbons on the surface of the black. These hydrocarbons probably are somewhat lower in refractive index than rubber, so that the net effect is a lowering of refractive index when this amount of channel black is added to rubber. To check this point, a sample of channel black was heated in a vacuum oven at 180° C. for 24 hours. When compounded in rubber, this sample of channel black had a refractive index 20 per cent higher than the same channel black before heat and vacuum treatment.

#### MECHANISM OF REFRACTIVE INDEX CHANGES

Two possible explanations for these observations are suggested. The first is based on the behavior of vulcanized rubber, which when stretched shows an

increase in refractive index because of molecular distortion. For example, elongating a vulcanized rubber-sulfur stock 300 per cent increases the refractive index from 1.5302 to 1.5350 ( $n_D^{25}$ ), and when the tension on the vulcanized sheet is released, the refractive index returns to its original value. In this investigation there was no change in refractive index when zinc oxide was incorporated in latex until the rubber was masticated in contact with the pigment. It was also observed that the refractive index of the rubber-zinc oxide stock approximately returned to the value of unpigmented rubber when zinc oxide was dissolved from the stock. These results suggest that the increase in refractive index can be attributed to the development of molecular strains induced in the rubber when masticated in contact with zinc oxide, and that these molecular strains are largely eliminated when zinc oxide is dissolved from the rubber. (It may be anticipated that with the removal of the pigment the original refractive index will be restored, and the fact that it does not occur may be due to a permanent deformation or set of the rubber molecule.)

The second mechanism suggested is that of the orientation of the rubber molecule at the pigment-rubber interface; in this case it would be anticipated that the orientation would cause an increase in the specific gravity of the rubber directly around the particles, which would be manifested in an increase in the refractive index. One could postulate that the increase would be related to the specific surface of the pigment, and the results on the several sized zinc oxides indicate this to be true. Holt and McPherson<sup>1</sup> found that the volume of a gum-rubber band decreases when elongated beyond 200 to 300 per cent—hence an increase in specific gravity on stretching. Rubber under tension shows an x-ray diffraction pattern indicative of orientation of the rubber molecules, first reported by Katz<sup>2</sup>. If these two experimental phenomena are related, one could logically assume that orientation results in an increase in specific gravity which is responsible for an increase in refractive index. These observations on cured gum-rubber compounds under tension gave rise to the theory involved in the second mechanism.

The data and suggested explanations are offered to stimulate discussion of the observed phenomena, and will be supplemented as further experiments are carried out.

#### ACKNOWLEDGMENT

The author acknowledges the helpful suggestions of A. H. Pfund of Johns Hopkins University and A. T. McPherson of the National Bureau of Standards, and the assistance of Norman A. Brown, who made the refractometer measurements. Thanks are also due The Goodyear Tire & Rubber Company for supplying the deproteinized rubber and Thomas Midgley, Jr., for furnishing the pure rubber hydrocarbon.

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# PRACTICAL EVALUATION OF COMMERCIAL RUBBER CARBON BLACKS BY X-RAY DIFFRACTION \*

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Of the dozen or more reinforcing agents used in the commercial compounding of rubber, carbon blacks are outstanding in their excellence<sup>4</sup>. Though no completely satisfactory theory has yet been forthcoming to explain the action of this material, the literature indicates that, among other factors, the size and shape of the ultimate carbon particles profoundly affect the characteristics of the rubber products obtained<sup>5</sup>.

Particle sizes of fillers and pigments are commonly determined by microscopic methods. Of those that have been suggested, the method of Gehman and Morris<sup>6</sup> is perhaps most widely accepted as reliable. All microscopic methods, however, are subject to the limitation of resolving power imposed by the relatively narrow range of wave lengths in the visible and near ultraviolet which can be used for viewing and photographic purposes. Further, no distinction can be drawn between ultimate particles and compact secondary aggregates from the microscopic point of view. Thus, there always exists the possibility that microscopic particle sizes represent groups of individual particles rather than the individuals themselves.

Although several investigations of the so-called "amorphous carbons" (any carbon product but those showing diamond or unquestionable graphite structures) have been carried out by means of x-ray diffraction methods<sup>1, 3, 7, 8, 10, 13</sup>, this tool has not enjoyed wide application in the determination of particle sizes and shapes of carbon blacks used in the rubber industry. Although some question has been raised concerning the approximate nature of x-ray results, this reluctance to employ x-ray diffraction methods is surprising, inasmuch as such methods not only suffer no restrictions due to limited resolving power (dimensions of the order of several Ångström units are commonly determined), but the results are absolutely independent of the presence, absence, or extent of secondary aggregate formation. It is the authors' opinion that such particle size determinations might be of considerable interest to the manufacturers of rubber products.

From a relatively simple measurement of the diffraction pattern, the sizes of ultimate particles lying in the submicroscopic range can be calculated by any one of several relations. Of these, two merit special attention. The first equation to be derived was offered by Scherrer<sup>11</sup>, though Seljakov<sup>12</sup> later generalized Scherrer's conditions and arrived at essentially the same conclusions:

$$B = K \frac{\lambda}{D \cos \theta} + b.$$

$B$  is the width at points of half-maximum intensity of the interference measured in radians,  $\lambda$  is the wave length of the parallel monochromatic radiation

\* Reprinted from *Industrial and Engineering Chemistry, Anal. Ed.*, Vol. 12, No. 2, pages 66-71, February 1940.



used,  $D$  is the extension of the primary crystallite in a direction normal to the set of crystal planes giving rise to the interference considered,  $\theta$  is half the diffraction angle as defined by the Bragg law, and  $b$  is an additive constant which depends for its value on the conditions peculiar to any one set of determinations. Scherrer obtained a value of 0.94 for  $K$ , while Seljakov obtained 0.92.

Somewhat later, von Laue<sup>9</sup> presented a more extensive mathematical treatment of the particle size question and offered the relation:

$$\eta = 0.0884 \left\{ B \cos \theta - \frac{1}{B} \left( \frac{\pi r}{R} \right)^2 \cos^3 \theta \right\}$$

in which  $B$  and  $\theta$  are defined as above,  $r$  is the radius of the cylindrical sample,  $R$  is the radius of the cylindrical camera, and  $\eta$  is a pure number related to the particle size by an expression involving wave length, lattice constants of the material, and particle dimensions. This latter equation, whose form depends on the crystal system of the substance under consideration, is simple for the  $h00$ ,  $0k0$ , and  $00l$  interferences of all unit cells which may be indexed in one of the orthogonal systems:

$$\eta = \frac{\lambda}{4\pi m a_i}$$

where  $ma_i$  represents the crystal extension in a direction normal to the diffracting family of planes. Von Laue's equation was derived on the assumption of absolutely divergent radiation emanating from a point in the circumference of the cylindrical film; but besides this difference, experimental conditions for the two methods are rather similar in nature.

#### EXPERIMENTAL X-RAY DIFFRACTION TECHNIQUE

The camera used in this investigation was the cylindrical camera commonly employed in this laboratory. The instrument was accurately calibrated and various radius values were calculated from exposures of pure graphite. Two sets of exposures were taken with two different types of sample. For one series, cylindrical samples were made by mixing the carbon black with a small amount of starch paste, compressing this paste in the bore of a short piece of glass capillary tubing, and allowing the resulting rod to dry in air after extrusion. The diameters of all such samples were carefully measured by means of a low-power microscope with a Filar micrometer attachment, and amounted to about 1 mm. For the other series, wedge samples were employed. The sample holder was split vertically along a diameter of the brass rod and the half nearer the incident beam was removed so that the resultant sample had the shape of a 30-60° right triangular wedge. Wedge samples were simply formed by merely pressing carbon black into the sample holder by means of a spatula.

Exposures were made of the wedge samples by means of collimated radiation from the strong pinhole of a copper anode Philips Metalix diffraction unit operated at 28,000 volts and 20 milliamperes. During exposure of the cylindrical samples, the collimator tube of the camera was replaced with a single pinhole [accurately machined to 0.25 mm. (0.010 inch) in diameter] located in the circumference of the circular film. In all cases, the radiation was filtered through nickel foil to remove copper beta and tungsten lines and render the radiation almost perfectly monochromatic. All patterns were registered on Agfa double-dipped x-ray film and exposures were regulated (8 to 10 hours) so that the

TABLE I  
PARTICLE SIZES, WEDGE SAMPLES, SCHERRER EQUATION

Sample	Average $W^a$ (002)	$D$ (002) $\text{\AA}$	Average $W$ (100)	$D^b$ (100) $\text{\AA}$
US1	7.93	13.5	6.95	17.9
US2	6.79	16.3	7.59	16.1
US3	6.94	15.8	7.30	16.9
US4	5.25	22.4	5.88	22.3
US5	6.84	16.1	7.24	17.1
US6	6.93	15.8	6.95	17.9
US7	6.57	16.9	7.75	15.7
US8	6.78	16.3	7.34	16.8
US9	6.53	17.0	7.24	17.1
US10	6.50	17.1	6.22	20.7
US11	6.75	16.4	7.42	16.5
US12	6.53	17.0	6.46	19.7
US13	6.97	15.7	7.24	17.1
G1	7.07	15.4	6.02	21.6
G2	6.89	15.9	6.67	18.9
G3	5.52	21.0	5.45	24.7
G4	7.49	14.4	7.47	16.4
G5	6.08	18.6	5.36	25.3
Graphite	1.16	CO	1.48	CO

<sup>a</sup>  $W$  indicates the width at points of half-maximum intensity of the interference as measured in mm. on the film. This is converted to  $B$ , the value in radians.

<sup>b</sup>  $D$  indicates the extension of the primary particle in the direction normal to the diffracting set of planes.

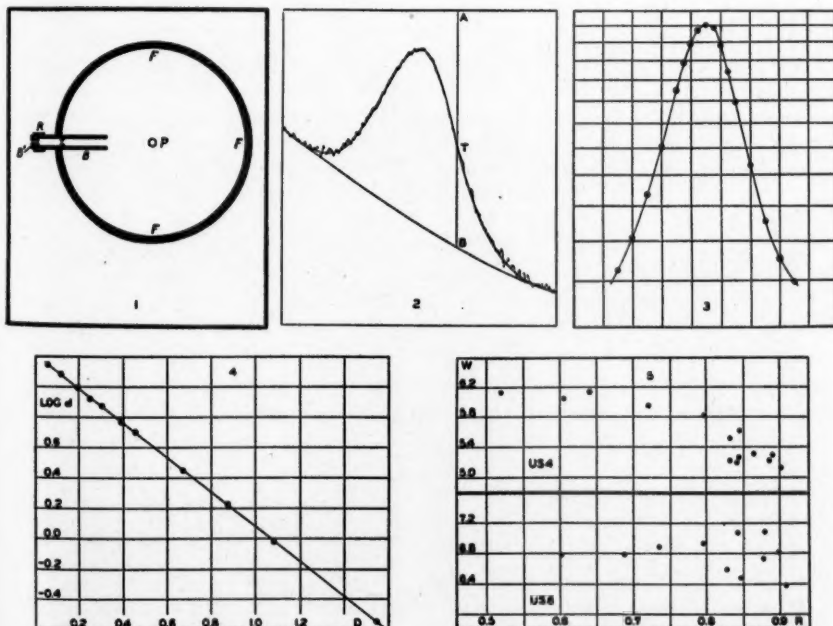


FIG. 1.

1. Schematic diagram of Debye-Scherrer camera.
2. Method of density calculation from microphotometer curve.
3. Intensity distribution of a 002 interference as determined from a microphotometer curve.
4. Log galvanometer deflection in microphotometer plotted as a function of film density.
5. Width at points of half-maximum intensity (in mm.) of 002 interference of US4 and US8 as a function of  $B$  (= ratio of intensity of monochromatic x-ray beam after passage through sample to initial intensity) to show effect of sample thickness.

maximum film density obtained did not exceed 1.5. This lies well within the range of linear response for such film.

All patterns were photometered with a Moll-type automatically registering microphotometer, using a silver-bismuth thermopile. Check calculations on specially prepared graded density plates showed the linear range of this instrument to extend far beyond any density value encountered in this investigation.

The procedure outlined above fulfills all the von Laue conditions for the cylindrical sample exposures (assuming that the very slight radiation absorption of the carbon black may be neglected without appreciable error), and all line widths obtained from patterns of such samples were used in the von Laue formula to calculate particle sizes. On the other hand, all wedge sample exposures fulfill the Scherrer conditions except for that of sample shape. Since the effect of sample radius (which really defines the incident beam of radiation in a Scherrer determination) is normally accounted for in calculation by the constant  $b$ , and since the radiation absorption of carbon black is practically negligible, it is to be expected that the use of a pinhole to define the beam in connection with a differently shaped sample would have little effect on the calculations except to give a different value to  $b$ . That this is true was shown by experiment. All line widths obtained from patterns of wedge samples, then, were used in the Scherrer equation to calculate particle extensions.

## RESULTS

X-ray patterns were taken of 18 samples of carbon blacks supplied by two large manufacturers of rubber products. All interferences were diffuse and of a nature to indicate very small particle size, which may be mathematically treated by radial distribution methods. In general, the lines were so broadened that only the 002 and 100 interferences were sufficiently developed to permit measurement of the half-maximum line width. In all cases, at least two good checks (better than the 5 per cent check commonly accepted in intensity work) of line widths were obtained; in many cases three good checks were obtained; and in a few cases where the first several determinations did not give good checks, exposures were continued until five or six good checks were obtained. Table I shows the averaged line width data obtained from the wedge samples and the resultant particle size values calculated by means of the Scherrer equation.

Table II shows line width data obtained from cylindrical samples and resultant particle sizes calculated by means of the von Laue equation. Since the cal-

TABLE II  
PARTICLE SIZES, CYLINDRICAL SAMPLES, VON LAUE EQUATION

Sample	Radius Mm.	W (002)	Average D (002) Å	W (100)	Average D (100) Å
US1 .....	0.446	7.69	12.6	6.99	14.2
US2 .....	0.498	6.76	14.3	6.26	16.2
US3 .....	0.498	6.62	14.7	7.40	13.0
US4 .....	0.496	5.59	17.7	5.72	18.0
US5 .....	0.516	6.56	14.8	6.36	18.5
US6 .....	0.467	6.65	14.4	7.41	13.7
US7 .....	0.486	6.62	14.5	7.95	13.3
US8 .....	0.452	6.66	14.7	7.58	12.9
G1 .....	0.427	7.11	14.2	7.48	13.4
G2 .....	0.483	6.71	14.3	6.41	15.6
G3 .....	0.516	5.72	17.3	5.43	19.2
G4 .....	0.453	7.56	12.7	5.84	17.9
G5 .....	0.513	6.20	15.8	5.02	21.0

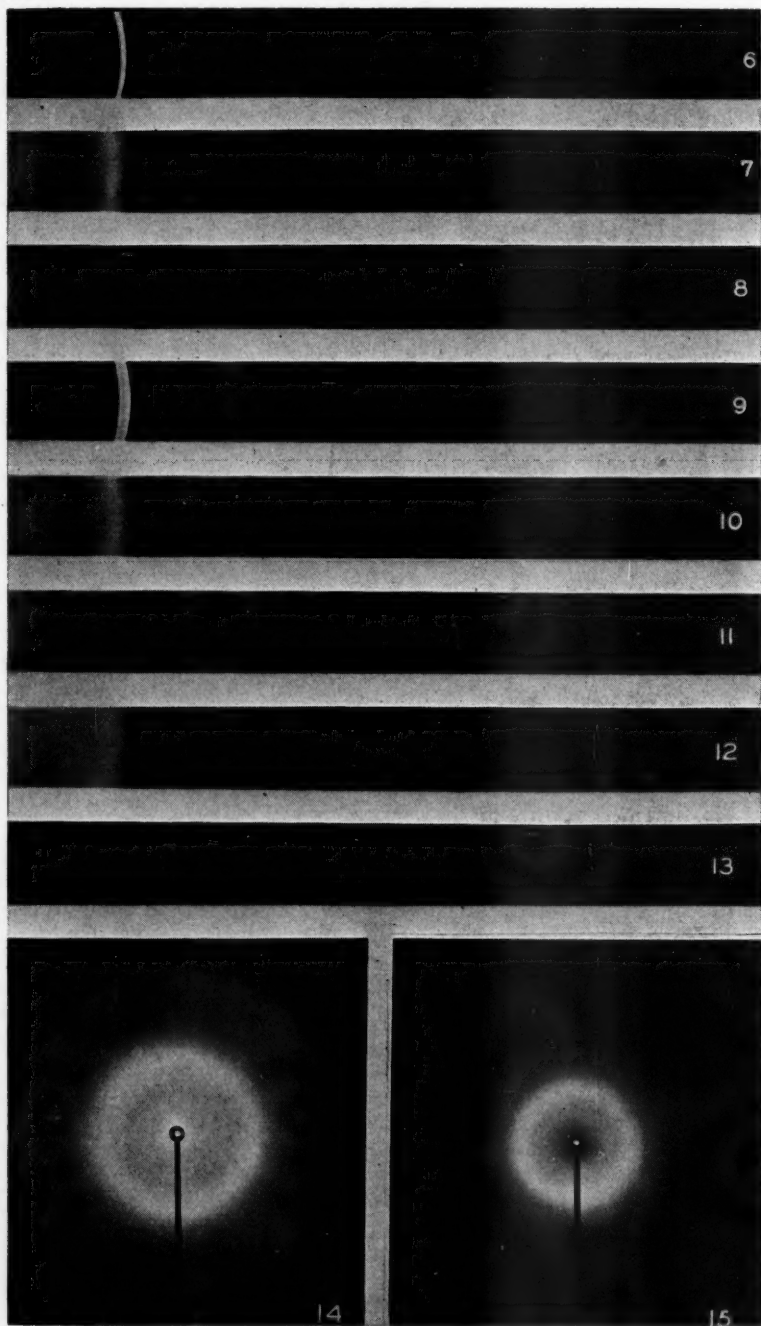


FIG. 2.—Diffraction patterns.

- |   |  |
|---|--|
| 6. Spectroscopically pure graphite, wedge sample.       | 10. Black US4, cylindrical sample.               |
| 7. Black US4, wedge sample.                             | 11. Black US1, cylindrical sample.               |
| 8. Black US1, wedge sample.                             | 12. Carbon black removed from rubber mix $M_2$ . |
| 9. Spectroscopically pure graphite, cylindrical sample. | 13. Zinc oxide filler.                           |
|   | 14. Carbon black US1.                            |
|   | 15. Pure rubber.                                 |

ulation depends on the value of the sample radius and since this quantity varies from sample to sample, line width data cannot be averaged, as they were in Table I. Instead, each calculation must be carried through to completion and averages taken of the final particle size values. For this reason, Table II shows only one representative line width with the corresponding sample radius, though the value given for the calculated particle size is the average obtained from all such values for the sample in question.

Comparison of the data of Table I with those of Table II was carried out by calculating the percentage deviation from the mean for each pair of particle sizes. For the 002 dimension, the percentage deviation of the two sets of values from the mean between them averages 5.46. The average deviation for the 100 dimension is 10.49. This less satisfactory value arises from the fact that all 100 interferences were less distinct than the 002 lines and were correspondingly harder to measure with accuracy.

Although in a few cases the calculated deviations seem to show considerable difference between particle sizes calculated on the basis of the Scherrer and von Laue methods for the same sample, in the writers' opinion these data constitute a rather good check. Cameron and Patterson<sup>2</sup> believe x-ray particle size determinations may be in error by as much as a factor of 2, while only one of the 26 comparisons of the sets of data above shows a deviation even approaching this figure. In view of this fact, the true average particle sizes of the 18 samples of blacks are probably very closely approximated by the data given.

Two facts in particular are at once apparent from these data. Assuming that the ultimate carbon particle is approximately a hexagonal right prism in shape, the value of the 002 extension is seen to be the prism altitude, while the 100 extension gives the base dimension between any two diametrically opposed apices. Consideration of the particle size data shows that the ultimate particles of commercial rubber carbon blacks have almost equal dimensions in the two principal crystallographic directions. This generalization is of particular interest when one recalls that the so-called active carbons commonly show a leaf-like or platelike structure with the base diameter amounting to several times the altitude<sup>7</sup>. Further, it should be noted that all particle sizes lie in a relatively narrow range. Thus, these samples indicate that the rubber industry has, by empirical and independent means, set up a standard of particle size as well as particle shape.

Samples G1 to G5, inclusive, were subjected to careful microscopic examination by another laboratory, and the particle sizes were determined by the method of Gehman and Morris. As was to be expected, these figures showed not the slightest agreement with the x-ray results. This result was expected from a casual inspection of the diffraction patterns. Ultimate particles with sizes given by this microscopic method (450 to 1120 Å.) should give distinct sharp-line patterns, while all diffraction patterns obtained were diffuse and ill defined. Table III lists the two inconsistent sets of data. The obvious rationalization of this discrepancy lies in the tendency of carbon blacks to form compact secondary aggregates and in the impossibility of microscopic observation of particles whose dimensions do not exceed 25 Å. Assuming that the secondary aggregates are roughly spherical in shape and that the microscopic particle size represents the value of the aggregate diameter, these data may be used to calculate the approximate number of ultimate particles per aggregate. Further weight is added to this interpretation by the fact that a series of zinc oxide samples gave concordant results for grain size by both microscopic and x-ray methods.



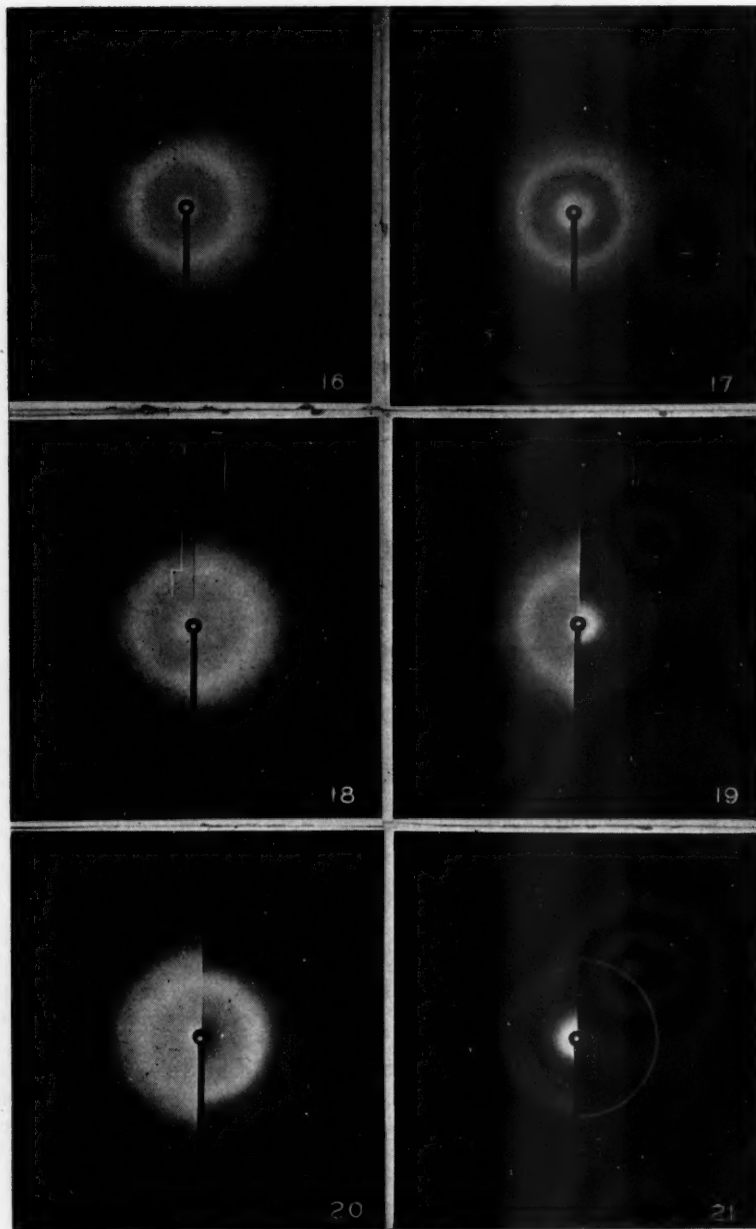


FIG. 3.—Diffraction patterns.

16. Black rubber mix  $M_2$ .
17. Double exposure of Black US1 and pure rubber.
18. Rubber mix  $M_2$  (right) compared with double exposure of US1 and rubber.
19. Rubber mix  $M_2$  (left) compared with US1.
20. Rubber mix  $M_2$  (left) compared with rubber.
21. Pure graphite (right) compared with US1.

It is obvious from Table III that x-rays and the microscope measure two entirely different structural units in the carbon blacks. The above calculations have been made on the basis that the primary particles were truly crystalline and of colloidal dimensions, and that the particle which appears in the microscope is a secondary aggregation of these units. There are, of course, other possibilities. Warren<sup>13</sup> has extended the powerful methods of dealing with liquids, glasses, and similar materials to the case of carbon black, in which no assumptions are involved as to the crystallinity of the material, but merely the distribution of atoms about any one atom calculated directly from the experimental scattering curve by the method of Fourier integral analysis. These results indicated definitely the existence of single graphite layers, in which the carbon atoms are arranged in the typical six-membered rings. Whether these single layers have definite orientation and position with respect to other similar layers, as is true in a graphite crystal, or whether carbon black is a mesomorphic form of carbon, could not be definitely decided from the experimental results. Warren's work, however, indicates that carbon black is a heterogeneous mix-

TABLE III  
COMPARISON OF MICROSCOPIC AND X-RAY DATA

Sample	Microscopic Size $M\mu$	X-Ray diffraction size		Particles per aggregate
		Altitude $\bar{A}$	Base $\bar{A}$	
G1	0.045	15.4	21.6	$3.2 \times 10^3$
G2	0.064	15.9	18.9	$9.2 \times 10^3$
G3	0.160	21.0	24.7	$6.4 \times 10^4$
G4	0.025	14.4	16.4	$8.1 \times 10^3$
G5	1.120	18.6	25.3	$2.4 \times 10^7$

ture of particles which range from single graphite layers up to graphite crystals several layers thick. An intense scattering at small angles is due to the difference between grain density and average density caused by the loose packing of the extremely small grains. Thus it is clearly evident that the maximum breadth of lines must be associated with these smallest subcrystalline particles.

Since the x-ray data indicate that in these rubber carbon blacks the particles are essentially equiaxed, on the average these must consist of a series of layers packed on top of each other, probably not in absolutely perfect array but in a distorted arrangement, as if a deck of cards were held firmly between the hands and twisted around an axis perpendicular to the surface. Thus distortion produces line broadening just as colloidal particle size does, and it is impossible to determine from these diffuse diffraction patterns just what contribution has been made by particle size and by a distorted structure. However, certain distinctive characteristics of the microscopic measurements are carried over into the x-ray measurements. Specimens G3 and G5 are thermal blacks with much larger microscopic particle size than the other 3 channel blacks formed at low temperatures from gas. The same distinction is observed in the x-ray data.

#### X-RAY EVALUATION OF BLACKS IN RUBBER MIXES

It would be an obvious advantage to be able to evaluate the particle sizes and shapes of blacks already compounded in rubber. Therefore, great effort has been expended to adapt the preceding methods to such mixes. It was first definitely established for several specimens that the diffraction pattern for the final cured

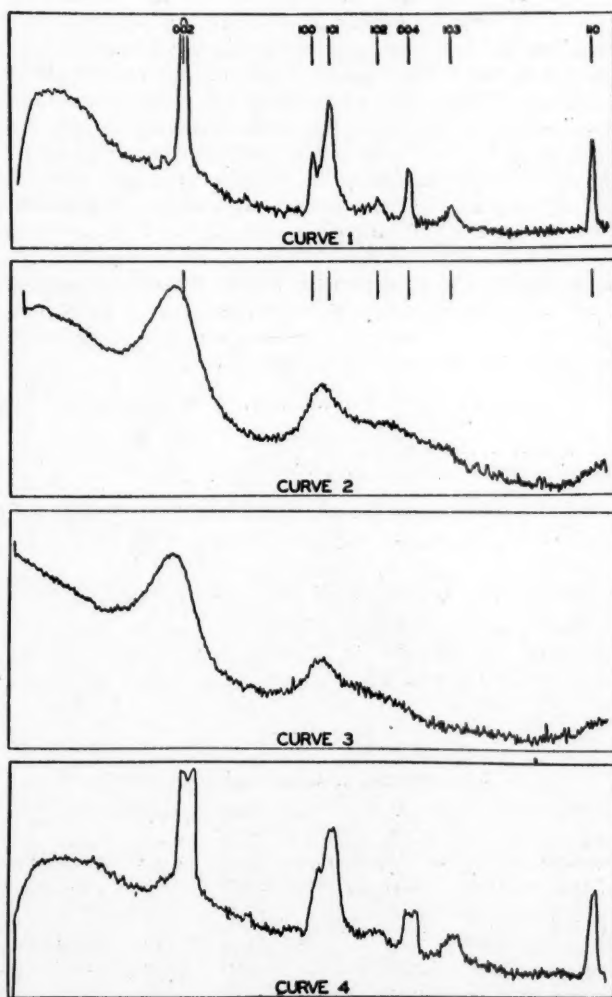


FIG. 4.—Microphotometer curves.

1. Trace of pure graphite (6, Figure 2).
2. Trace of US4 (7, Figure 2).
3. Trace of US4 (10, Figure 2).
4. Trace of graphite (9, Figure 2).

mix could be duplicated exactly by superposing on the same film the patterns of rubber alone and the black alone. Thus there is no evidence whatever that the mix is anything more than a physical dispersion, even if adsorptive forces may be very powerful. These patterns show at once that the carbon black strongest interference 002 is so seriously obscured by the halo of unstretched rubber that measurement of the width at points of half-maximum intensity of the former is impossible. However the corresponding width of the weaker 100 interference may still be measured with sufficient accuracy to permit a fair estimate of the particle size. Although this interference is capable of showing only one dimension of the particle, the particles of all blacks investigated are so nearly the same shape and so nearly equidimensional in the two principal directions that an approximation of particle size can be made from a single measurement. Separate films for sample M1 gave for this interference widths at half-maximum intensities of 8.71, 8.80, and 8.75; for M2, 7.13 and 6.93.

The alternative method is to reduce the rubber content by swelling, refluxing, and solution of the rubber and separation of the black by high-speed centrifuging, to a point where the strong 002 interference of the black will be resolved. The following values are obtained for sample M2.

W (002)	Av. W (002)	W (100)	Av. W (100)
8.05 .....	7.79	7.41	7.36
7.53 .....	—	7.32	—
Original black used in M2.....	7.85	—	7.16

Thus the agreement in values for the black alone, the rubber mix, and the black extracted from the mix is very satisfactory.

#### RELATION BETWEEN PARTICLE SIZE AND OTHER PROPERTIES

Even if all the commercial blacks are similar in particle size and have nearly the same dimensions in the two principal crystallographic directions, it is of interest to present in Table IV a summary of measurements with these specimens

TABLE IV.

#### PROPERTIES OF CARBON BLACKS

Sample	Apparent density *	Particle Area <sup>b</sup> A. <sup>2</sup>	Total surface Sq. m./g.	Active surface <sup>c</sup> Sq. m./g.	DPG adsorption <sup>d</sup> Mg./g.	Ratio 4:5 *	Tensile strength <sup>f</sup>	4% modulus <sup>g</sup>	Shore durometer
US1 .....	0.067	3130	1563	117.2	26.48	4.43	—	—	—
US2 .....	0.138	2913	1518	23.2	10.05	2.31	4678	2280	66
US3 .....	0.316	3085	1487	29.2	10.95	2.68	4990	2530	70
US4 .....	0.253	5584	1090	4.8 <sup>h</sup>	1.40	3.43	4064	765	55
US5 .....	0.277	3161	1466	22.8	1.92	11.90	—	—	—
US6 .....	0.277	3383	1440	27.4	9.80	2.80	4680	2365	64
US7 .....	0.216	2863	1501	21.4	7.55	2.84	4098	2415	66
US8 .....	0.161	3097	1473	29.0	9.16	3.16	4453	2370	66
US9 .....	0.171	3256	1428	24.8	6.93	3.58	4320	2260	62
US10 .....	0.227	4361	1289	9.6	1.35	7.10	—	—	—
US11 .....	0.239	3076	1496	23.2	6.82	3.40	4203	2365	67
US12 .....	0.071	3501	1391	25.6	4.95	5.18	—	—	—
US13 .....	0.253	3123	1483	30.0	10.28	2.92	4637	2345	65

\* Determined with great care in a modified Scott volumeter.

<sup>b</sup> Calculated from x-ray data in Table I, assuming right hexagonal prisma.

<sup>c</sup> From methylene blue adsorption and Paneth's data for area covered by 1 mg. of methylene blue in a monomolecular layer. Analysis with Cenco-Sheard-Sanford Photometer.

<sup>d</sup> Adsorption of diphenylguanidine (accelerator) per gram of carbon.

<sup>e</sup> Variation in surface adsorption of different materials (methylene blue and diphenylguanidine).

<sup>f</sup> Carbon black in conventional tread compound at optimum cure, tensile strength in Scott machine.

<sup>g</sup> Same stock, modulus measured by stress-strain machine on ring-shaped test-piece.

<sup>h</sup> Contained more than 2% extractable material.

on apparent density, particle area and total surface in square meters per gram, calculated from the x-ray data, the active surface calculated from methylene blue adsorption, diphenylguanidine adsorption, and three mechanical proper-

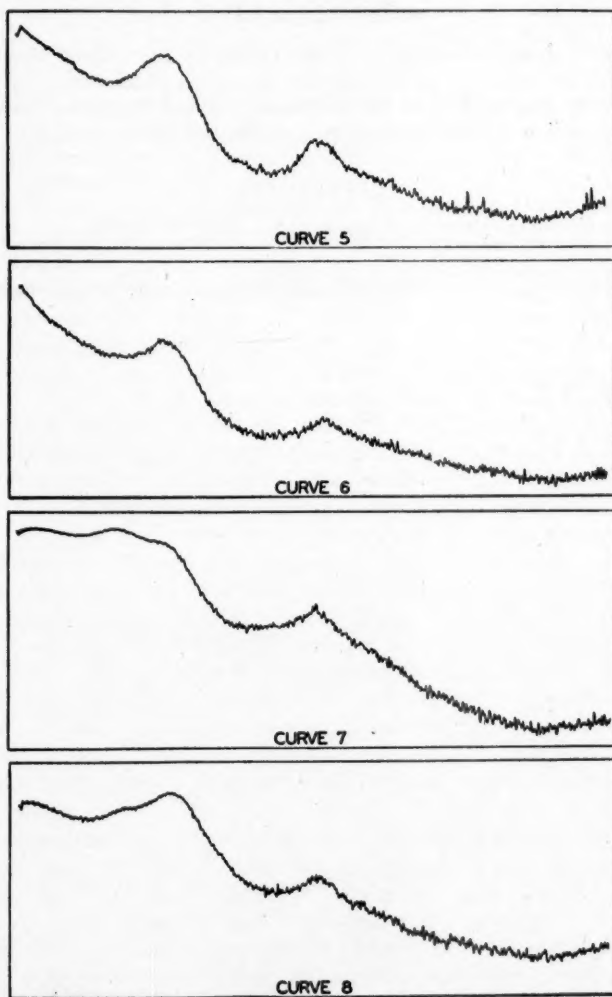


FIG. 5.—Microphotometer curves.

5. Trace of US1 (8, Figure 2).
6. Trace of US1 (11, Figure 2).
7. Trace of black rubber mix M<sub>2</sub>.
8. Trace of carbon from mix M<sub>2</sub> (12, Figure 2).

ties of cured tread stock containing these carbons. Especially noteworthy is No. US1, which is extremely fluffy, has by far the greatest active surface, and also has the greatest departure in particle shape from equiaxed grains. This is in agreement with the contention that the most highly activated carbons have flakelike shapes. Carbon US4 is anomalous, but this was found to be due to



the presence of more than 2 per cent of extractable tar. When this was removed, the purified residue was comparable with the others. The same was true of US10.

#### ACKNOWLEDGMENT

The writers' thanks are due to R. H. Gerke of the United States Rubber Company for the donation of 13 samples of carbon blacks used by that company and to S. D. Gehman of the Goodyear Rubber Company for his gift of 5 samples of carbon blacks, previously investigated microscopically by him.

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## MIXING AND MOULDING WITHOUT MASTICATION \*

F. H. COTTON AND W. F. HODSON

Since the inception of the rubber manufacturing industry, it has been general to plasticize rubber by milling before incorporating fillers and setting the material in its final shape by vulcanization. As it is now known that the size of the rubber molecule is reduced by a form of cleavage (involving oxidation) during mastication, it has appeared desirable to investigate means of converting the raw material to the finished product without the degrading intermediate stage of mastication.

The proportion of rubber goods placed in the vulcanizing pan in the form of hand-made and shape articles has fallen to an almost insignificant figure since the beginning of the century. Our industry has, of late years, benefited from the phenomenal developments which have occurred in the art of moulding, particularly since the miraculous rise of that bird of brilliant plumage born in the fire of 1914-1918: the Phoenix of the Plastics Industry.

Synthetic resins are usually supplied in powder form, ground and mixed with fillers and pigments, ready for direct shaping in the highly polished metal moulds in which the composition is simultaneously cured. It is natural that many attempts should have been made to produce raw rubber in a powder or crumb form simulating the physical conditions found most satisfactory in the plastics trade. From time to time efforts to mould and vulcanize such powder have been reported, and it is recollected that Fordyce Jones exhibited, at a meeting of the Institution of the Rubber Industry in 1936, some small flexible saucers moulded from a rubber powder compound. However, replying in discussion to a question regarding direct moulding from rubber powder (*Trans Inst. Rubber Ind.* 12, 139 (1936)), Fordyce Jones said he was not fully satisfied with the results he had obtained, because of lack of proper equipment, which would be expensive. He remarked: "Here is a field for work which appears to have a promising future."

The attractive nature of the proposition and its inherent difficulties were stressed last year by Porritt and Parris ("Encyclopedie Technologique du Caoutchouc," p. 383), who stated: "An advantage of rubber powder as compared with ordinary rubber in mass form might seem to be in the compounding of the rubber. It has been suggested that the rubber powder and compounding ingredients could be stirred together and mastication avoided. So far, however, this expectation has hardly been realized, as without mastication it is difficult to effect sufficiently intimate mixing of the rubber powder and the other ingredients. Moulding powders have been prepared, but they appear to require the addition of a considerable proportion of a fluxing agent, as for example naphthalene, to ensure intimate contact between the rubber and the vulcanizing ingredients."

This paper records experiments which have convinced the authors of the practicability of moulding suitably compounded rubber powder by an injection method.

\* Reprinted from *The Rubber Age* (London), Vol. 20, No. 11, pages 317-321, January 1940.

## 1. THE RAW MATERIAL—RUBBER POWDER

When the work was begun, the only rubber available in powder form was that made by the Stam process and supplied by the Rubber-Latex-Poeder Cie. of Holland. Stam powdered rubber resembles finely ground semolina in appearance, and is capable of passing through a 200-mesh sieve (size of aperture 0.076 mm. sq.). In its production, treated latex is sprayed by means of a centrifugal sprayer into a current of hot air. One type of sprayer described has a diameter of 32 cm. and is rotated at 15,000 rev. per minute. In the latest form the centrifuge is trumpet shaped and attached to a tube passing through the bottom of a drying chamber. Through this tube latex is conveyed to the spray. A current of hot air is blown up around the sprayer so that the ejected particles of latex become quickly dried and are carried away through an opening at the top of the drying chamber.

In the earlier patents covering this process, dextrin in the proportion of 6 to 12 per cent of the latex is recommended as a protective colloid to prevent agglomeration of the dried rubber particles; but the hygroscopic nature of this material renders it unsuitable as an addition for rubber to be subsequently consolidated, vulcanized, and employed under conditions which rubber goods are frequently called upon to withstand. Many means were subsequently tried for preventing ready self-adhesion of the dried latex particles; but it is believed that the powder used in the experiments herein described was made from latex to which had been added an ammoniacal solution of zinc phosphate. It has been suggested that this reacts with the serum components of the latex and results in the formation of a non-adhesive layer round the rubber particles. The powdered rubber employed in the investigation was free running and showed no tendency to agglomerate. It could even be ground in a ball mill without danger of the individual particles cohering.

## 2. MIXING AND MOULDING TECHNIQUE

To test the truth of the prevalent belief that powdered rubber is difficult to mould satisfactorily, and also to acquire familiarity with the reactions of the material, the first experiments were made with a mixing of powdered rubber produced with the aid of a laboratory mortar and pestle of porcelain. It was thus found quite simple to reduce the following mix to an apparently homogeneous powder:

	Parts by weight
Rubber powder .....	100
Sulfur .....	2
Vulcafor D.A. ....	1
Kadox zinc oxide.....	5

The rubber showed no tendency to ball or stick together, as might have been expected. The mix was bulky and of low apparent density. The powder flowed with such ease that it proved impracticable to charge a normal flash-type rubber mould (such as a ring mould for producing Schopper test discs) with sufficient rubber to compact and fill the mould in one operation. It became obvious that some form of plunger mould would be necessary, the cylindrical gravity of which could be filled with the powder to be subsequently compressed by means of a piston into a disc much smaller in volume than the uncompressed powder.

Fortunately a number of small plunger moulds complying with these requirements was available. A weighed quantity of the above mix was charged into

one of these cylindrical plunger-type moulds and simultaneously compressed and vulcanized at 153° C. (307° F.: 60 lbs. per sq. in. steam pressure) in a hydraulic press under a pressure of 4 tons per sq. inch of the plunger face. On opening the mould it was found that, although a skin of continuous rubber had been formed on the surface of the moulded disc, the interior consisted of compressed powder which could easily be disintegrated by rubbing between the fingers. It was surprising that the rubber powder was able to support such a load at this temperature without showing marked tendency to fuse together in the center. The experiment furnished spectacular proof of the success with which the individual particles of rubber had been protected and isolated from intimate contact during the process of manufacture.

Following this initial experiment, numbers of mixings were made by the same simple procedure, employing the same basic combination, together with additions of the following substances in an attempt to find a suitable softener, or a means of otherwise inducing cohesion:

Mineral oil.

Zinc stearate.

Naphthalene (recommended in formulas submitted by Rubber Latex Poeder Cie.)

Lead peroxide (as a powerful oxidizing agent to soften the rubber by oxidation).

Red lead.

In each of these experiments a similar result was obtained. A surface skin was formed on the moulding, where actual fusion of the rubber particles seemed to have occurred; but inside this skin the rubber remained in the discrete form. Lead peroxide exerted such a powerful oxidizing action that the rubber became exceedingly sticky, but this did not successfully unite the mass. The moulding broke easily, and the stickiness of the rubber was merely apparent through the formation of minute web-like threads at the moment of rupture.

Failure of typical softeners to produce the desired result led to a trial of the following expedients:

1. Increasing the pressure during moulding to 10 tons per sq. in. of plunger face.
2. Vulcanizing under these conditions for 5 minutes at 186° C. (=368° F.; 155 lbs. per sq. in. steam pressure).
3. Vulcanizing under the same conditions for 30 minutes at 186° C.
4. Use of other accelerators, including zinc diethyldithiocarbamate (Z.D.C.), zinc isopropylxanthate (Z.P.X.), mercaptobenzothiazole (M.B.T.).

All these treatments failed to produce a homogeneous vulcanized rubber sample of satisfactory physical strength. Of the series, the drastic treatment of subjecting the mix to 30 minutes vulcanization at 186° C. under 10 tons per sq. in. hydraulic pressure produced the best results.

#### FIRST EXPERIMENTS IN INJECTION MOULDING

In all the later experiments recorded above, it was noticed that the spew forced up under great pressure between the plunger and the internal face of the mould cavity was not merely coherent, but remarkably strong and elastic; in fact, the spew exhibited just those features it was desired to impart to the moulding as a whole. It was surmised that the internal friction caused by forcing the powdered rubber between the opposing faces of the plunger and the mould cavity had mechanically ruptured the protective skin around each rubber par-

ticle; thereby facilitating that rubber-to-rubber contact sought for, which mere mechanical pressure, even aided with softeners, had failed to achieve.

Consideration of this observation suggested that if the powdered rubber mixes were forced into the mould under great pressure through a small hole, they might be subjected to such a shearing influence during passage through the orifice that the rubber particles would be burst and fitted for immediate cohesion. It was at once appreciated that sections of the plastics industry employ this technique in the manufacture of what they term "injection mouldings." A predetermined quantity of a thermoplastic moulding powder is placed in a heated cylinder which is then closed by means of a piston. This piston, actuated by hydraulic or other power, squirts the heat-softened material through a fine nozzle into a cold mould, where it immediately sets, ready for removal.

We have to thank Messrs. Fraser and Glass, Ltd., of Woodside Lane, North Finchley, N.12, for their cooperation in enabling us to carry out preliminary experiments in two presses actually engaged in the mass production of injection mouldings.

Quantities of the following mixes were prepared for testing-out in the factory. In each case a vulcanizing mix (in the nature of a master batch) was first prepared by mixing vulcanizing ingredients with a relatively small quantity of rubber powder in a mortar with a pestle, and then the necessary proportion of this vulcanizing mix was compounded intimately by hand with further rubber powder. The whole was then rubbed through a sieve to ensure uniformity.

	Parts by weight
<b>Mix A:</b>	
Rubber powder .....	475
Vulcanizing mix (a).....	62.5
	<hr/> 537.5
<b>Vulcanizing Mix (a)</b>	
Rubber powder .....	100
Zinc oxide (Kadox).....	100
Sulfur .....	40
Z.D.C. ....	10
	<hr/> 250
<b>Mix B:</b>	
Rubber powder .....	475
Vulcanizing mix (b).....	82.5
	<hr/> 557.5
<b>Vulcanizing Mix (b)</b>	
Rubber powder .....	100
Zinc oxide (Kadox).....	100
Sulfur .....	40
Z.D.C. ....	10
Zinc stearate .....	80
	<hr/> 330
<b>Mix C:</b>	
Rubber powder .....	475
Vulcanizing mix (b).....	82.5
Whiting .....	500
Vulcafor Green L.S.....	10
	<hr/> 1,067.5



Experiments were made with two types of mould. The first produced a thin-flanged insulating bobbin for a wireless transformer, and the second a more massive wheel with grooved periphery clearly illustrated in the photograph (see Figure 1).

The first mould was admirably adapted for testing the capacity of a rubber powder mix to flow under pressure, as the mix was only introduced to the mould through four small apertures indicated by the tiny pips left on the inner faces of the squares constituting the near ends of the central holes exposed in the photograph. It was also felt that the thin section of this moulding would facilitate rapid vulcanization and exaggerate any distortion which might characterize the injection method of introducing rubber to the mould.

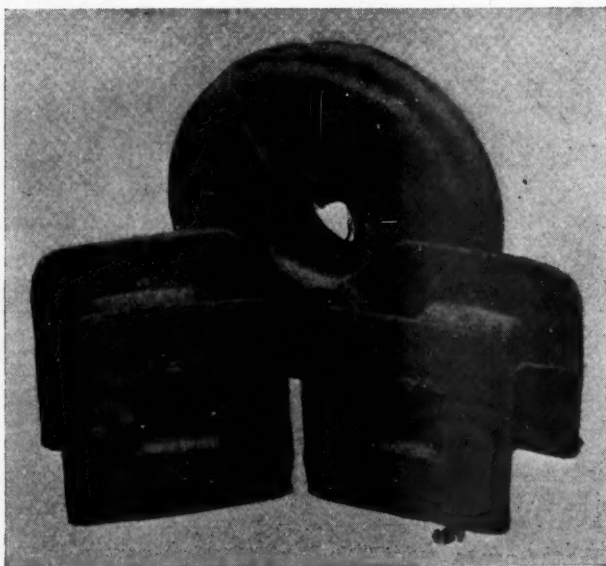


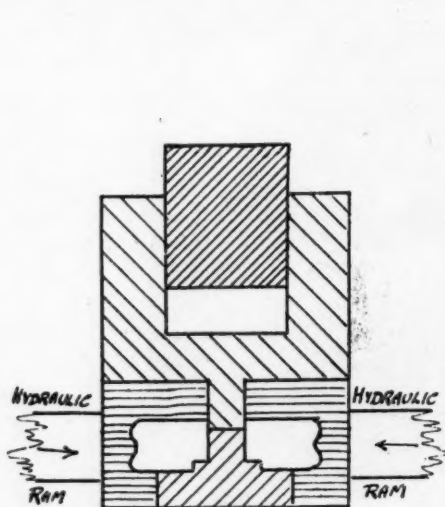
FIG. 1.—Following an experiment with two types of mould, the second produced "a more massive wheel with grooved periphery" (shown here).

It was found possible to inject mix A so as to fill all parts of the bobbin mould; but with many of the mouldings produced, the flanges were appreciably distorted and were obviously non-homogeneous in composition, as should be visible from the mottling apparent in the lighter photograph. It was not practicable accurately to measure the temperature of the injection cylinder and mould, but mouldings were produced at approximately 130° C. and removed after periods varying from two to ten minutes. A qualitative indication was obtained that the temperature of the injection cylinder and the mould was of importance in determining the appearance, cure and freedom from distortion of the finished article.

Mix B, containing zinc stearate, was unsatisfactory. It had been anticipated that the zinc stearate might act as a flux and facilitate fusion and cohesion of the rubber particles; but this did not appear to occur, and the mouldings containing the ingredient developed numerous white specks.

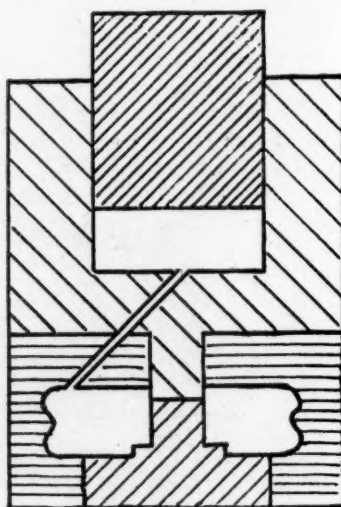
The whiting in mix C (colored green and therefore showing darker in the photograph) had the advantage of reducing the contraction and distortion which occurred when the injection moulding was removed; but the mixing was insufficiently intimate to give a strong product. It was apparent that the hobbin containing whiting was not homogeneous in composition. Numerous light colored particles were visible in its surface, and the outer edges of the lower flange had so little cohesion that they could be easily rubbed away.

A portion of mix A was injected, from another press, into a mould, the two major portions of which were held in contact by hydraulic pressure, as indicated in the drawing (see Figures 2a and 2b) to produce an object resembling a pulley wheel (see photograph). Examination of the finished moulding indicated that the rubber powder had been forced in two converging streams around the



Front Elevation.

FIG. 2-A.



Side Elevation.

FIG. 2-B.

center of the mould. The leading edges of these two streams of rubber may have undergone partial vulcanization during injection: whether or not this occurred, the two streams failed to unite perfectly, leaving a weak section of incoherent rubber at that portion of the moulding diametrically opposite to the point of injection of the rubber powder mix. A series of mouldings was made under varying conditions, but always with a similar result. Another significant feature of each of these mouldings was a marked distortion particularly apparent as a swelling around the point of entry of the rubber mix to the mould (this may be seen on the photograph). The flow lines discernible on the moulding suggested that the swelling just referred to occurred immediately after removal from the mould, and was due to an elastic after-effect of the strains set up in the rubber while forced to flow in the mould. The effect may be likened to grain in a calendered sheet. Similar distortion was frequently experienced during subsequent work, and is considered one of the more serious problems to be overcome before injection moulding of rubber powder compositions can be perfected.

## EXPERIMENTAL INJECTION MOULDING APPARATUS

The preliminary work carried out at a factory specializing in the injection moulding of plastic materials was sufficiently encouraging to warrant the construction of an experimental injection moulding apparatus.

The form adopted is illustrated in Figure 3. It consisted of a stainless steel cylinder A, let into the upper surface of a steel disc-mould B, to the cavity in which the injection cylinder communicated by means of a small hole of 1/32 inch bore. Sliding in the cylinder A was a plunger enlarged at the top as shown, intended for contact with the upper platen of a hydraulic vulcanizing press. The powdered rubber mix was charged into the cylinder A, where it was compressed by the plunger after inserting the whole in a vulcanizing press. The rubber powder mix was consolidated under pressure and forced through the

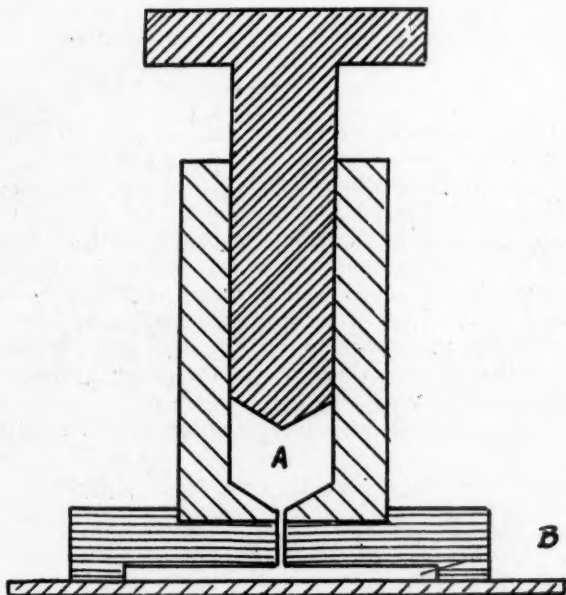


FIG. 3.

small hole into the cavity B to form a rubber disc of the standard size employed in preparing Schopper tensile ring test-pieces. The bottom of the mould consisted of a plate which contacted with the lower platen of the steam-heated hydraulic press, and could be removed for releasing the cured disc.

The hydraulic press employed was able to exert a pressure on the rubber in the cylinder, through the interposition of the plunger, of 25 tons per sq. inch.

## OBSERVATIONS: MODIFIED TECHNIQUE

Speed was originally considered so essential to any satisfactory injection moulding process for rubber, that experiments were confined to mixes such as A containing ultra-accelerators. This is now known to have caused the failure of all the earlier experiments with the injection apparatus described. Discs moulded under pressure from such mixes distorted seriously on removal from

the mould. They would not lie flat; their centers expanded and led to the disc assuming a saucer shape. Nevertheless, rubber discs moulded in this apparatus were far more coherent and strong than those produced in earlier experiments employing a plunger-type mould.

It was rightly surmised that the distortion of these early injection mouldings was a result of vulcanization occurring before the rubber had flowed to the extremities of the mould. With the following mix a satisfactory disc, practically free from distortion was obtained after injection and vulcanization for 15 minutes at 60 lbs. per sq. in. steam pressure (applied to the lower face of the mould only).

	Parts by weight
Rubber powder .....	100
Sulfur .....	3
Kadox zinc oxide.....	5
D.P.G. ....	1.5
	<hr/> 109.5

From the resulting cured disc a Schopper ring was punched. This was tested on the dynamometer and gave a tensile strength of 110 kg. per sq. cm. (=1,575 lbs. per sq. in.) and an elongation at break of 670 per cent. This was far in excess of anything achieved in previous experiments.

To improve the dispersion of vulcanizing ingredients with the rubber powder, tests were made in which the complete mix was placed in a dry ball mill and subjected to grinding for 24 hours. This produced much more intimate mixing. The rubber powder showed no tendency to ball together or form lumps. It is believed, however, that when ultra-accelerators were incorporated they began to cause vulcanization of the rubber during the mixing period, and resulted in serious distortion of the moulding.

This difficulty was overcome by employing a delayed action ultra-accelerator in the following mix:

	Parts by weight
Rubber powder .....	100
Sulfur .....	2
Zinc oxide .....	5
Vulcafor D.A.U. ....	1
	<hr/> 108

Discs of this mix were injected and vulcanized for 3, 5 and 10 minutes, respectively, at 153° C. (60 lbs. per sq. in. steam pressure). The resulting discs were not seriously distorted, despite the fact that heat had been mainly applied to one of their surfaces only. Tests on the Schopper dynamometer gave the following results.

Vulcanization	Breaking stress (kg. per sq. cm.)	Elongation (per cent)
3 min. at 153° C.....	135.9	360
5 min. at 153° C.....	60.2	318
10 min. at 153° C.....	52.7	277

It is highly significant that the highest tensile strength was obtained after three minutes' vulcanization, although heat was only transmitted to the lower face

of the disc. It is believed that the enormous stresses exerted on the rubber during injection to the mould cause such tremendous frictional losses, as the consolidated powder is forced through the orifice, that much heat is produced. It is suggested that this frictional heat serves to raise the mass of the rubber mix to a relatively high temperature at the moment of filling the mould. Therefore, substantially uniform vulcanization commences immediately.

This would appear to constitute an advantage of the injection moulding process, viz., that the rubber mix may be automatically raised to the vulcanizing temperature throughout its bulk at the moment of injection.

#### CONCLUSIONS AND RECOMMENDATIONS

The preliminary experiments described indicate the remarkable potentialities of the injection method of moulding rubber articles, whether produced from mixes of powdered or masticated rubber.

Employing rubber powder made by the Stam process, intimate mixing with vulcanizing ingredients and fillers is essential, and may conveniently be achieved with simple apparatus by ball milling the ingredients. The necessity for heavy rubber machinery of the orthodox type is eliminated.

It is desirable to employ an accelerator of relatively low activity, or a delayed action ultra-accelerator. With very fast accelerators, vulcanization begins either during mixing of the powder or while being forced from the injection cylinder to the mould. Such premature vulcanization leads to serious distortion.

It is believed that the stresses to which a compressed rubber powder compound is subjected during the process of injection moulding are sufficient to rupture the individual rubber particles, to ensure cohesion, and promote satisfactory dispersion of compounding ingredients.

It is confidently asserted that results superior to those instanced herein could be achieved with an injection moulding device designed to facilitate uniform heating of both top and bottom of the mould cavity. It is also felt that a careful study of the effect of changing the injection pressure and the size of the injection orifice might yield valuable information.

The success attending these early experiments warrants extending the investigation to new types of rubber powder (cf. *Rubber Age*, 19, 335 (1938)).



# PRODUCTION OF DECORATIVE AND ORNAMENTAL RUBBER PRODUCTS \*

J. P. GRIFFITHS and C. R. PINNELL

It is proposed to deal with the production of rubber goods which can lay claim to being decorative and ornamental, not according to their classification in a sales catalog, but according to the machines which produce them.

## CALENDERING

One of the difficulties in a works handling rubber qualities ranging from pure gum stocks to the more heavily compounded variety, such as flooring, is to obtain sheets of the same thickness across the width. The wider the sheet the more difficult this becomes. With perfectly cylindrical rolls, the pressure of the rubber bank at the nip will cause the roll to bend, so that a sheet of rubber coming from between such rolls will be thicker in the middle. This variation is overcome by making the rolls a little thicker in the middle by only a few thousandths. However, the amount of bending depends on the type of stock being calendered, so that one calender cannot produce sheet of even thickness from all types of mixings. The greater thickness of the rolls in the middle compared with the ends is referred to as the camber. When the machine is under load, the camber corrects the bending so that the effect is equivalent to using perfectly cylindrical rolls that do not bend. Unless a firm has more than one calender for different types of stock, there is always one class of mix which cannot be the correct thickness right across the sheet. For many classes of goods this variation is not important, but for sheets of rubber intended for flooring to be cut to tiles and pure gum sheet to be cut to thread, it is obvious how important the question of uniform thickness becomes. One cannot expect mechanical pressure during vulcanization to correct this fault or, if it does, other effects are spoilt. For example, the marble pattern on flooring may be spoilt by a sideways flow of rubber under a powerful press, especially where considerable variation was present in the thickness of the calendered sheet. A recent method of correcting camber is to swing the top bowl of, say, a three-bowl calender, so that the axis of one bowl is at an angle to the one immediately underneath. The rollers are, of course, perfectly cylindrical, and only have to be swung through a few degrees.

Some plain pale colors in flooring qualities are more difficult to run than marbled effects. Where one requires very fast curing qualities, thus introducing a risk of scorching, there is a tendency to run too cold, and although there are no crow's-foot marks, one gets long spear-point-like markings of slightly lighter tones, which do not disappear during cure. To overcome this, higher temperatures must be used, and where a rapid cure is essential the more modern accelerators have to be employed; these are usually mixtures of two or more different chemical constituents which together give high critical temperatures, often higher than any of the individual constituents. The fast vulcanization is that required on modern continuous vulcanizers now used. The mechanical pressure on these machines is quite high, but it cannot, of course, correct any

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 15, No. 2, pages 95-107, August 1939.

variation in thickness between one part of the uncured rubber sheet and another, and where thin parts occur the rubber will be porous and undercured. These machines will not cure the rubber mixing properly unless it is pressed with the full pressure against the heated surface, and this again stresses the importance of perfect calendering in all its details, such as evenness of warming-up, plasticity of the mix and feeding the calender. This latter detail now calls for a considerable amount of skill in design owing to the guards now essential under the Factories Act.

The production of marbling on the calender calls for a high degree of skill to keep a pattern uniform and reproducible at will. The rubber is fed to the nip with the different colored mixes rolled up together, either as headers or stretchers, as required by the pattern, and where the final thickness required is greater than that which can be run in one sheet on the calender, the doubling can be done on this machine, if the equipment allows, or on a separate doubling machine. In the latter case one has the advantage of being able to select the best portion of the marbling for the top. A considerable amount of waste may be made when marbling, if care is not taken at the beginning and end of a run to secure a marbling true to type, particularly when doubling on the calender.

Another kind of calender sheet rubber, which can be regarded as ornamental, is the purer type which is dressed with finishes for such articles as aprons, baby pants, and dress shields. Some of these are thin, in the region of five-thousandths of an inch, and translucent, and must be run on faultless calenders. There must be no surface blemishes on the rolls, and no gear marks showing. All signs of trapped air must be absent. This latter condition can be obtained by building-up from thinner coats run consecutively or simultaneously, and also by correct feeding to and temperature of the rolls. The passage of the rubber through more than one nip removes the air to a considerable extent, but for rapid output of perfect sheet, calenders with as many as five rolls are used. The construction of the five-bowl calender has already been described<sup>1</sup>. The advantages of such a calender are that fine sheet can be run in two coats and so reduce the risk of blemishes, and with a quicker output. With some types of mixes, sheets greater than certain thicknesses cannot be run in one ply, so that increased output with a five-bowl calender is readily apparent.

If calender grain is not removed from sheet rubber, trouble is often experienced when hand-made goods are cured, by the alteration in shape which occurs when the strain is released from the rubber by the heat or solvent. If the temperature of the calender bowls is somewhat higher than that of mixing, the tendency to get the grain effect is minimized. The effect can also be removed by placing the sheets, after cutting to the required lengths, on a chest heated with hot water; or by lapping the continuous sheet in cloth on a drum and immersing in hot water for about half an hour. The temperature in each case should be about 80° C.; higher temperatures, although not scorching the bulk of the rubber, tend to form a scorched skin over the surface of the sheet, which reduces its tack when joining to other uncured rubber in the making-up. This latter effect occurs principally with qualities containing organic accelerators. Where sheet rubber has been rolled up in a liner on the calender, it is better to roll it off into another cloth before it is quite cold to remove the risk of a slight retraction in width at the expense of a slight increase in length and thickness. The thickness of the sheet must be controlled continuously, either by hand, in which the operative has to cut off pieces from time to time for examination with a thickness gauge, or by devices through

which the sheet rubber passes as it leaves the calender. These devices, such as the Schuster gauge, automatically alter the setting of the rolls, or leave it for the operative to correct any errors indicated.

With a train of cooling rolls and a chalking device, the sheet rubber for such articles as colored aprons can be dealt with on mass-producing lines. As the sheet rubber comes from the calender, cooled and chalked with the appropriate finish, it is passed immediately to zinc-topped tables. When one layer in the length required has been run on the table the sheet is cut across, the following rubber is placed on top of the first layer and so on, until the correct number of layers is obtained; this pile of sheets is then removed on its zinc sheet, and the following rubber built up into another pile. The pile of sheets is cut to the required shape and vulcanized in air after placing another sheet of metal on top to keep them in place and produce flat sheets. Long lengths of colored solid sheeting can be produced by curing it in steam, when lapped on itself, or with interleaving paper. Precautions must be taken to exclude condensed water. The calendered sheet can also be cold-cured in sheet form or made up into articles, and vapor cured in tumblers<sup>2</sup>. Thin rubber of contrasting colors can be stuck to the goods, for example, frills and tapes on aprons, before cure. For the quick application of such decorative strips, there are suitable machines on the market, together with hammering machines for the rapid production of good seams.

Where one cannot work in the manner just described, smooth surfaces can be obtained on one or both sides of a sheet by running from the calender on to single or double faced liners. The rubber is left till cold, chalked, stripped from the liner and used for hand-made goods, such as cushions, sponge-bags and toys. Such goods, according to the mixes used, can be open steam, hot air- or cold-cured. The latter can be performed by vapor cure in a tumbler or on shapes placed in a suitable chamber into which the sulfur chloride vapor is passed. A shiny finish can be obtained on vapor-cured goods by using no dusting powder, and mixing a little nitric acid with the sulfur chloride before vaporizing. Lacquers and varnishes can also be employed for the same purpose. These will be referred to again later.

Dull and mat finishes can be obtained by dusting with suitable powders such as lycopodium, maize flour or the like, and hot air- or cold-cured, the thickness of the rubber deciding the type of cure.

Such goods as bathing shoes can be built up by sticking the sheet rubber to aluminum formers with a rubber solution and vulcanizing in hot air. The decorative effects are obtained by using motifs and strappings in contrasting colors, or the use of previously embossed rubber. Shoes made of smooth rubber can be made more ornamental by the pebbling effect, mentioned later under dipped goods. The sections for building up such articles as shoes are cut out by shaped steel cutters on clicking machines. Many thicknesses can be cut by one blow, although many manufacturers still prefer cutting out the parts by hand.

A more recent method of cold curing to obtain a cured result with good aging is by the use of dibutylamine. This consists of mixing in with the rubber the sulfur and accelerator, such as mercaptobenzothiazole, and making the goods in the usual way. A solution is then prepared of dibutylamine and a further accelerator such as zinc ethylphenyldithiocarbamate in benzene. When this solution is applied to the rubber mix, sufficient extra accelerators are thereby added to produce rapid vulcanization at low temperatures. The

methods of handling this process and the plant used are identical with that required for ordinary cold-curing with sulfur chloride in carbon disulfide. The curing will take place on its own if left, or it may be assisted by placing the goods in a warm place. Proofed fabric, dipped goods, or any articles usually cured by sulfur chloride in solution may be made by this method.

Mention has been made of vulcanizing sheet rubber on continuous vulcanizers. These machines usually consist of a steel cylinder with a very smooth surface 3 feet or more in diameter, the cylinder being capable of working with an internal saturated steam pressure of up to 80 lbs. per sq. in., and being rotated with its axis in a horizontal position. The rubber is pressed against the surface of a cylinder by an endless belt. Obviously rapidly curing qualities have to be used, but accelerators with a high critical temperature are best. By using such accelerators, one avoids the risk of the rubber setting before the full mechanical pressure is applied. If one has not avoided this condition, the result is a pock-marked surface and a sheet containing air blisters or even pores. If the surface of the cylinder is plated and kept clean, highly polished flooring can be obtained. Embossed effects can also be obtained by the use of an engraved cylinder in place of the smooth one. Another method of obtaining an embossed surface, but still using the smooth surfaced cylinder, is to cure the rubber next to it, but to run an embossed matrix between the rubber and the endless belt. The embossed matrix must be of a flexible heat-resisting material that can be used many times.

#### SPREADING MACHINES

Another machine in a rubber factory, used to a considerable extent for producing decorative or ornamental effects is the spreading machine. Proofed fabrics that have been vulcanized by the cold, heat or self-curing processes are used in large quantities for clothing, such as raincoats, bags to hold such articles as sponges, and powder puffs. The finish or feel of such products can also be considered as part of the ornamental effect; these are usually produced by the addition of factice to the mix and starchy dusting powders on the surface. Similar materials are also used for curtains by printing on the surfaces before cure with rubber mixes in solution made with quick-drying solvents. The printing can be done on the spreading machine by using an embossed metal roller conveying the printing solution, the solution lying in the trough formed by the roller and a stiff leather doctor. The pressure of the doctor on the roller controls the amount of solution left on the raised portions producing the pattern, and these almost immediately come in contact with the material to be printed. By this method only one color can be applied at a time, but the simultaneous printing in more than one color can be performed on the more stereotyped forms of printing machines. Effects with aluminum and bronze powders are usually applied by the spreading machine type of printing, the solvent being dried off in the usual way on the spreading machine. Embossed effects for imitation leatherette are usually applied by heavy embossing calenders before varnishing and air curing. The machine for the air cure of varnished proofing cannot be of the type shown in Morris's paper<sup>1</sup>, because in this machine the sheet passes up and down over rollers so that the face of the goods comes in contact with the bottom rollers. This would damage the varnished surfaces. The air cure for such materials has to be arranged so that the festoons are carried bodily through the machine. The mechanical method for forming festoons is the same as that used in other industries, such as in the manufacture



of wallpaper. There are many quick-drying varnishes on the market suitable for such processes. For producing the cheaper unembossed leatherette materials on the market, shellac is still the most used polishing material. Each proofer has his own recipe for the manufacture of his polish. The chief troubles to be guarded against are that the polish should not rub up white, and that any plasticizers should not give a tacky feel. Floral designs on proofed curtains for shower baths, etc., are often actually the printed patterns on the fabric showing through a cold-cured transparent pure-gum proofing. When proofing any material which has been printed in colors, care must be taken to determine that the coloring materials on the fabric will not cause rapid deterioration of the rubber, copper should not be present to a greater extent than 40 parts per million, and they should not be soluble in the rubber or solvent, and so bleed into the proofing. The colors should also be capable of withstanding sulfur chloride. Spread fabric imitating suede leather is also produced on the spreading machine. This is obtained by allowing specially prepared comminuted colored silk or wool or cotton fibre to fall on the freshly spread and tacky rubber surface, just behind the spreading gauge. The cloth is then beaten to cause the fibres to take up the vertical position. The cloth passes down the spreading table, and the excess fibre is removed from the surface of the sheet at the back drum of the spreading machine. The material is then air-cured.

#### EXTRUSION MACHINE

Extrusion machines do not readily lend themselves to the production of ornamental effects. However, striped effects can be obtained on machines specially designed for the purpose. To produce this effect, an ordinary extrusion machine has a special type of head, which is really another small extrusion machine at right angles to the major machine. As the tube is extruded, the smaller machine forces a different colored rubber through holes in the die of the larger machine. The size of the holes and the relative plasticities of the two qualities being used determine the width and depth of the stripes. This method produces a seamless tube. The so-called hand-made tube or a tube with a join down it can be made in any design by first preparing sheet rubber with a built-up or marbled pattern. The sheet of correct thickness is cut to strips and the edges made tacky with solution. The strips are then pulled through draw-plates which bend the rubber round into a cylindrical form, and at the same time press the edges together to make a perfect joint. The coiled-up tube can then be cured in open steam. Tubing of a neutral color can be colored in short lengths by being dipped in, or painted with, rubber solution and vulcanized by sulfur chloride as vapor or in solution.

#### EMBOSSING CALENDER

Continuous lengths of solid rubber sheet in any color can be embossed by passing through embossing calenders. These usually have one roller covered with an engraved pattern which is easily interchangeable, or other types are built with interchangeable shells and not interchangeable rollers. These rollers are usually solid and not heated, so that the rubber must be of a suitably plastic nature to be capable of receiving the pattern and keeping it during vulcanization. If the rubber is not in such a condition, the pattern disappears during heat vulcanization, since the rubber has only been temporarily deformed under



strain, which is released by the heat. Small areas of sheet, suitable for making into articles such as tobacco pouches, can be embossed in presses which are maintained at not more than 220° F., in order to avoid skin scorching. These sheets are then clicked out, made up into pouches by hand, and cured on formers in open steam. To prepare plates for such presses, white metal is run on a suitable matrix. When the impression has become faint or damaged, the metal can be re-run at a low cost.

#### APPLICATION OF LATEX

The applications of latex to the production of rubber goods generally sounds simple, and for making a few articles on a small scale, the processes are not particularly difficult, but when larger scale operations are attempted, troubles occur. Variations in the latex, variations in the temperature and humidity of the air, all have effects which are far reaching if the manufacture is to be carried out continuously throughout the year. Conditioned work-rooms can deal with the weather, and bulking can deal with the latex if the production is on a sufficiently large scale.

One of the simplest methods of using latex is to pour it on to a flat surface and allow it to dry to form a sheet; one method of making decorative aprons is to pour the latex mix on to sheets of glass with a decorated surface, confining the latex by strips of wax-paper and stacking the sheets of glass in racks until the latex is dry. When the latex is stripped off, the pattern of the glass is transferred to it. Instead of allowing the latex to dry by exposure to the air, the impermeable glass surface may be replaced by an absorbent surface.

The use of plaster of Paris moulds for the production of rubber articles from latex has an extensive use in what is sometimes termed the cold-casting process. Generally the latex mix is suitably compounded and then destabilized or agglomerated by the addition of such materials as calcium formate. By this means the individual latex particles flock together, forming aggregates which do not choke the surface of the plaster but allow a considerable thickness of rubber to be built up.

Any decorative surface from which it is possible to take a plaster cast may be used as a prototype for the rubber article. Quite apart from the surface configuration, it is possible to apply other surface effects; for example, several similar latex mixings of different colors may be roughly mixed and then poured on to the plaster to give a marbled effect. By spraying a latex mix at a grazing incident angle upon a configured plaster mould, and then applying a different colored latex, striking effects are produced, and the decorative effect due to the surface is greatly enhanced.

The moulds are not confined to flat surfaces, but may be used to make hollow rubber articles, such as play-balls, and shoes, and, by using different colored mixes, marbled effects may be obtained, or, in the case of open moulds such as are used for shoes, one colored mix may be applied first and when the required thickness is obtained, this is emptied out and replaced by another of different color, the final article having different colors inside and out. In the case of such articles as balls, the moulds are usually rotated, since it is impracticable to fill the mould completely.

The actual making of the moulds must be under strict control or else the shrinkage will vary and cause the final product to show varying differences from the master. Similarly the mix must be carefully controlled, or again varying shrinkage will cause irregularity in the product. Generally the mixings are

checked each half-day to see that they are capable of giving the correct thickness when left in the moulds for fixed times.

Instead of putting the latex inside the moulds, the reverse can obviously be applied to the production of decorated articles, and all types of fancy goods may be prepared by dipping. Various dipping methods may be used; for example, one may use porous or glazed forms, the latter are essential for transparent goods. The porous forms may work by simple removal of the water from the latex due to their structure, or a vacuum may be applied to the inside of them to increase this effect. Either the porous forms or the glazed forms may be coated with a suitable coagulant which will give an increased thickness of deposit. It is possible to prepare heat-sensitized latex mixings, and thick deposits can be obtained by dipping heated formers into such mixings. Particularly with heat-sensitive and also with ordinary dipping mixings, provision should be made for keeping the dipping tanks cool. It is also necessary to maintain a standard viscosity, particularly if the dipping is performed automatically by machine, and it may also be necessary to keep the mix stirred with a low-speed stirrer.

When a highly compounded mix of high viscosity is used for dipping, it is often found that the dip crazes on drying, particularly by heat. Crockett<sup>3</sup> makes use of this generally annoying tendency to make ornamented shoes and other articles, by first dipping a form in a heavily compounded colored latex mixing, and then drying to cause the deposit to crack in a very diversified manner. A second coat of a similar mix having less fillers and a different color is then applied by dipping or spraying, and when the article is finally stripped, the second color appears through the cracks in the first.

An interesting form of surface adornment makes use of surface tension<sup>4</sup>. A former with a surface consisting of miniature ridges and valleys is dipped into a colored latex mixing of 8 to 15 per cent total solids. After the excess is drained off, the residual latex, under the influence of surface tension, forms a meniscus in each valley, causing a greater thickness on the hillsides than at the bottom of the valleys. On drying out, the result is a darker shade at the top of the slopes and a lighter shade below. After partial drying, a uniform layer of latex is applied to form a backing and when dry, the whole is stripped from the form.

A method for pebbled dipped latex articles has been patented<sup>5</sup>, using a precisely similar method, although sulfur chloride cures are not to be recommended for latex. Another method for latex goods<sup>6</sup> produces the crinkled surface without recourse to curing, by dipping a former into latex, then into 25 per cent acetic acid, on the surface of which floats a quarter-inch layer of benzene. Another method<sup>7</sup> uses equal amount of acetic acid and alcohol as a coagulant, followed by dipping into toluene.

Grained effects may be produced in a different manner, by causing local coagulation and consequent contraction by dehydration, or syneresis, by treating the latex surface with solid materials or droplets of solution which will cause coagulation by chemical action or dehydration. The results may be used as masters to produce forms for straight dipping<sup>8</sup>.

#### RUBBER SOLUTIONS

Rubber solutions may be used to form an article completely, or to give a surface effect. Only a few decorative articles, such as grained or pebbled gloves, are formed entirely from rubber solution. The surface of the glove is both

ornamental and useful in obtaining a firm hold where a smooth surface is ineffective. With both rubber solution and latex, a favorite method is to swell the rubber with a solvent which causes it to wrinkle, and then to fix the wrinkling by curing while still swollen. For example, a glove form is dipped in rubber solution to the required thickness, and the surface lightly cured in a sulfur chloride vapor cure; it is then dipped in solvent, which swells the rubber under the cured surface giving a wrinkled effect and then in a solution of sulfur chloride, which fixes the wrinkling. By varying the initial vapor cure and the time of immersion in the solvent, fine or coarse wrinkling can be obtained at will.

Many articles, particularly such surgicals as enemas, spray bulbs, and tubing, are given a pleasing appearance by coating with an enamel. The article is dipped into a rubber solution of the appropriate color. To remove the tack, the enamelled article used to be dipped in sulfuric acid, but nowadays the enamel is generally cured in sulfur chloride, and if properly carried out the result has a high finish. It is possible to modify the surface before cure to give a softer velvet finish, but in either case the results are attractive. The enamel is generally purer than the base mixing, and care must be taken in selecting the mixes so that, when the article is distorted, the surface does not form into unpleasant looking ridges. Naturally the mix must be allowed to stand for some days to allow all air to rise to the surface and any particles of foreign matter to sink to the bottom. The dipping may be performed by lowering the articles into the solution, or by raising the solution to cover the articles; in either case the speed must be uniform and so controlled that no drops are formed.

### MOULDING

Only thin articles with a decorative surface may be produced by dipping on a suitable form to show the same design as the form; if slightly thicker they may be turned inside out. Much thicker articles cannot be produced in this manner, but they may be produced by moulding. The cold-casting process has already been mentioned, but the moulds may suffer from several faults, which although possibly of small consequence for purely utilitarian articles, are generally fatal when a decorative effect is aimed at. For example, small air bubbles formed when making the mould will result in a pimply rubber casting, because a faulty plaster mould cannot really be made good; sometimes in drying, the moulds warp, giving uneven seams. In use, crystals of calcium sulfate may develop in the surface, causing defects in the surface of the rubber, and a mould which gives a highly polished effect at first gives progressively rougher castings with each use. During use, the moulds gradually slow up and the time of absorption has to be increased; this point has to be watched, or else thin articles will be obtained. If the moulds are scrapped at an early stage to surmount these difficulties, then naturally the costs increase. These defects are overcome by using heated metal moulds together with a heat-sensitized latex, as, for example, in the Kaysam process. If a decorated surface is given to the metal, it should last almost indefinitely with proper care, although the initial cost will be much higher than the plaster mould. However, although production from a sample in moderately large quantities may be started cheaply in a few days using the cold-casting process, it is more expensive and slower using heat-sensitized latex. It is worth while noting that the moulds for use with heat-sensitized latex are most suitably made from aluminum, and that since cast aluminum is often porous, wrought aluminum should be used<sup>2</sup>.

## ELECTRODEPOSITION

The electrodeposition of rubber from latex has no counterpart in pre-coagulated rubber, and it has many possible uses in the manufacture of decorative articles. At the moment it is not used to any great extent for this purpose, but in America it is used for the production of labels and decorative motifs for rubber goods by depositing rubber electrically on a previously prepared zinc plate to give the required design, and then superimposing a thin sheet of contrasting color on the deposit and semi-curing the whole when it is ready for application. The cost of the plates is rather high, particularly if the design is intricate.

An article which might be described as decorative is the Charnaux corset, which has hundreds of tiny holes disposed in a decorative manner. These are produced by depositing rubber on a hollow electrode which has ebonite inserts, the rubber being deposited upon the metal only. Two corsets are produced, one on the outside and the other on the inside of the anode.

Although many of the facts are known regarding the electrodeposition of rubber, a considerable degree of skill is required to obtain anything but the simpler articles.

## SPRAYED RUBBER

Another obvious use of rubber in a fluid state is to spray it; on account of their high viscosity, rubber solutions are not well adapted for spraying, and this process is chiefly confined to latex. To get good results, it is essential that the air from the compressor should be entirely freed from moisture and oil, or else unsightly blemishes are likely to occur. Even if the original mixing contains air bubbles, spraying generally removes these, giving a homogeneous product. Mixings for spraying must be stable to friction, or else the spray muzzles will choke and, unless deliberately desired, they must not tend to coagulate as the fine drops pass through the air. As stabilizers, a mixture of glue and casein has been recommended, but with Revertex, saprotin is used successfully.

One of the simplest methods is to spray through stencils; for example, one may spray a colored latex through a stencil on to a partially dried or wet latex sheet of a different color<sup>10</sup>, or first spray through a stencil on to a suitable backing. The loss of ammonia on spraying causes quick coagulation, which prevents perfect coalescence of the rubber into a smooth form, and results in the formation of a grained or beaded surface. Instead of ammonia, complex salts of zinc and ammonia may be used; these form coagulants by loss of ammonia<sup>11</sup>.

## SELF-SETTING LATEX

A further method of using latex is to make it self-setting by adding to it a material that will combine with water, such as cement. A material suitable for wall or flooring covering is made by incorporating into latex mixings, marble chips, fragments of glass, pieces of colored vulcanized rubber, etc. These may be mixed with the latex before application, or the latex mix may be applied first and, while still moist, the pieces are pushed into the surface. The mixes used for the purpose usually contain aluminous cement, which does not coagulate latex like ordinary Portland cement, and may be added to Revertex stabilized with saprotin, simply by sieving it in while stirring the latex.



If the particles are added to the mix, the surface is smoothed out with a wet trowel and, after the mix has set and been allowed to dry for about two days, the surface is ground and polished to expose the large particles, giving a terrazzo effect. The mixings for this need fairly careful adjustment as often the base contracts on setting and drying, and shows cracks.

Hastings<sup>12</sup> found that cracking of a similar material used for roads could be prevented by the addition of a gelling agent and a delayed-action coagulant. Sodium silicate was added as the thickener and sodium silicofluoride as the delayed-action coagulant, the coagulant being added immediately before application of the mix.

Some investigations on the interaction between cement and latex<sup>13</sup>, showed that a considerable rise in temperature indicated some kind of chemical reaction between cement and water. The effect of various protective colloids on the structure is also reported, and the experiments indicate that saponin prevents the cement particles building up into a continuous cement structure, thus giving a rubbery product.

There is a method for marbling paper whereby drops of various colors are allowed to fall from the tines of forks on a thin solution of Irish moss, and the spots of color are then raked over to form a marbled disposition upon the surface. The paper is then laid on top of this and on removal it takes up the colors, to give the effect often seen inside the covers of ledgers.

A similar effect may be used for decorating rubber goods. For example, a tank is divided into two compartments by a partition which reaches down for a short distance from the top. The tank is filled with water, and drops of thin various colored rubber solutions are distributed over the surface, as described for paper. The rubber articles, for example, from freshly coagulated latex are passed slowly through the colored layer floating on top of the water and thereby take up the colors to give a jazz effect, and are withdrawn through the clean water on the other side of the screen. In a somewhat similar process, the colors are dropped in at one end of a trough and are carried along its length by a stream of water; such articles as play-balls are held in a pair of tongs and are dipped into the water and withdrawn with a twisting movement.

Another method of applying jazz patterns, particularly with toy balloons, is to prepare solutions of certain water-soluble dyestuffs, particularly those which are soluble in dilute acetic acid, and then screw up the balloons in a small bag and boil them in the solution. Where the solution has access to the balloons, dyed patches are formed. The balloons are bagged up again and boiled in another color, whereby more dyed patches are formed. The process can be repeated as often as desired, and the colors are fixed by rendering them more or less insoluble by a final boiling in dilute alkali.

The authors wish to express their thanks to the Directors of Messrs. William Warne & Co., Ltd., for permission to publish this paper.

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# RUBBER AS ANTIVIBRATION MATERIAL \*

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## 1. INTRODUCTION

The idea of using rubber as a material for the damping and insulation of mechanical vibrations is not new. That this application of rubber has had no great scope up to now can be ascribed to a combination of circumstances: on the one hand there are unlimited varieties of rubber, concerning which rubber manufacturers publish no technical data, which can be relied on for specific projects; on the other hand there is a lack of knowledge of the behavior of rubber by builders themselves. In these circumstances it seemed desirable that the Rubber Foundation should endeavor to assist builders in this respect, and to this end a basic research into the vibration characteristics of rubber has been carried out. We shall report here on several points resulting from this investigation. Moreover we shall also discuss what can be expected of rubber, how it can be most economically used, and what advantages it shows over other materials.

Rubber at the present time is unjustly considered an untechnical material, yet of late the rubber industry has made enormous advances. Types of rubber of different hardnesses can be made which for practical purposes are ideally elastic, since they are in no way plastic, and their durability is so great that a piece a few centimeters thick has almost an unlimited length of life, for example, ten to twenty years, without any appreciable change in properties. The generally feared aging symptoms in rubber for technical applications are now of secondary importance. These are actually not more than a surface oxidation which can injure thin rubber articles of poor quality in a comparatively short time, but has no influence on thicker articles. However, this does not mean that adequate attention should not be given to this question. For such a purpose one must use a superior type of rubber, from the best material, vulcanized by an expert.

## 2. THE ELASTIC BEHAVIOR OF RUBBER

It follows from the general theory of vibration insulation that in principle one can use any springy material. The choice is determined by a number of considerations. Every material has its characteristic advantages and disadvantages. Before going into this, however, we should like to speak generally of the elastic behavior of rubber.

We shall consider first:

### *a. Rubber under compression and tension.*

The predominating characteristic which, in our view, is all too little known in technical circles, is that rubber is practically incompressible. The compressibility is of the same order of magnitude as that of water. A solid piece of rubber derives its so-called compressibility (in the case of one-sided compression), almost entirely from the possibility of lateral spread. Soft rubber

\* Reprinted from the *Mededeelingen van de Rubber-Stichting, Amsterdam*, No. 16, February 1940, 12 pages.

which is completely hindered in lateral spread conducts itself as a completely rigid material. This is the case in the application of a thin rubber layer between steel plates, which is thus a wrong one. For the moment we shall consider rubber which is not laterally obstructed, namely, in the form of a solid cylinder which, with respect to the pressure plates, can glide freely under compression (for instance, through the application of lubricants) and, in the case of tension, is considered long in comparison to the diameter. In analogy to a steel spring we may therefore speak here of a spring constant, *viz.*, the force per unit of compression. Since all deformation takes place at constant volume, at 50% compression the compressed surface becomes twice as great, while the height becomes twice as small. The simplest supposition is that we are still in the range where the elastic properties of rubber do not depend on the elongation. If this is true, then at 50% compression we find a spring constant four times greater than with an undeformed cylinder, namely, a factor 2 in consequence of the decrease in height and a factor two for the increase of the area. This is found experimentally to be true. The non-linear behavior of rubber under compression is therefore illusory and is explained by a constant elasticity modulus.

Under tension, the reverse appears. Starting with a constant (intrinsic) elasticity modulus, one would expect that the spring constant would decrease with lengthening, for instance, a factor 4 at 100% elongation. This, contrary to expectations, was also confirmed by experiment. However, with instinct as our guide, we involuntarily observe the behavior at elongations (100% to 700%) where the simple considerations are no longer valid, due to the appearance of an appreciable stiffening.

It is easy then to see that when one takes into consideration the changes in form, and works from a constant elasticity modulus, a non-linear relation is found between force and compression (tension). Under these hypotheses, the curve which indicates the relation between force and compression (tension) appears on close study to be a hyperbola.

In Figure 1, two of the hyperbolas are drawn. The solid line refers to soft rubber, and the dotted line to a somewhat harder sort. The relative compression  $y$  (defined as decrease in height, given as fraction of the total original height) is plotted against force of compression  $x$ . Since  $x$  is defined as the force per unit of surface of the original surface,  $x$  is equal to the force of compression except for a constant. The drawn hyperbola goes through point  $y = -0.25$  at  $x = -2$  kg. per sq. cm., and through this one point is therefore entirely determined. The dotted hyperbola is determined through point  $y = -0.25$  at  $x = -8$  kg. per sq. cm. and is connected with the drawn hyperbola because at each value of  $y$  the corresponding value of  $x$  of the dotted curve is four times greater than that of the heavy curve. We may now introduce a material constant, for which we choose the tension in kg. per sq. cm. original surface at 25% elongation. In accordance with the usual rubber terminology, we shall call the modulus at 25% elongation  $S$ . If one (see Figure 2) plots in all hyperbolas the relative compression  $y$  against the reduced compressional force  $x/S$ , then they all coincide. We thus come to the conclusion that for technical applications only one single compression and tension curve of rubber need be given, based on a single material constant  $S$ .

Thus from Figure 2, the relative compression is read at once by the compressional load and the kind of rubber ( $S$ ). For vibration insulation purposes, however, it is not enough to know only the static compression. Even more important is knowledge of the elastic behavior of the mounted machine when

loaded. This is also simple to derive from the graph. The quantity we seek is the spring constant in loaded condition, and this equals  $dx/dy$  — except for a geometric factor (height divided by area of the non-loaded rubber spring) which is to be found from the inclination of the pressure curve at the point of the static load. To simplify this still further, the line  $\sqrt{\frac{dx/dy}{S}}$  as function of

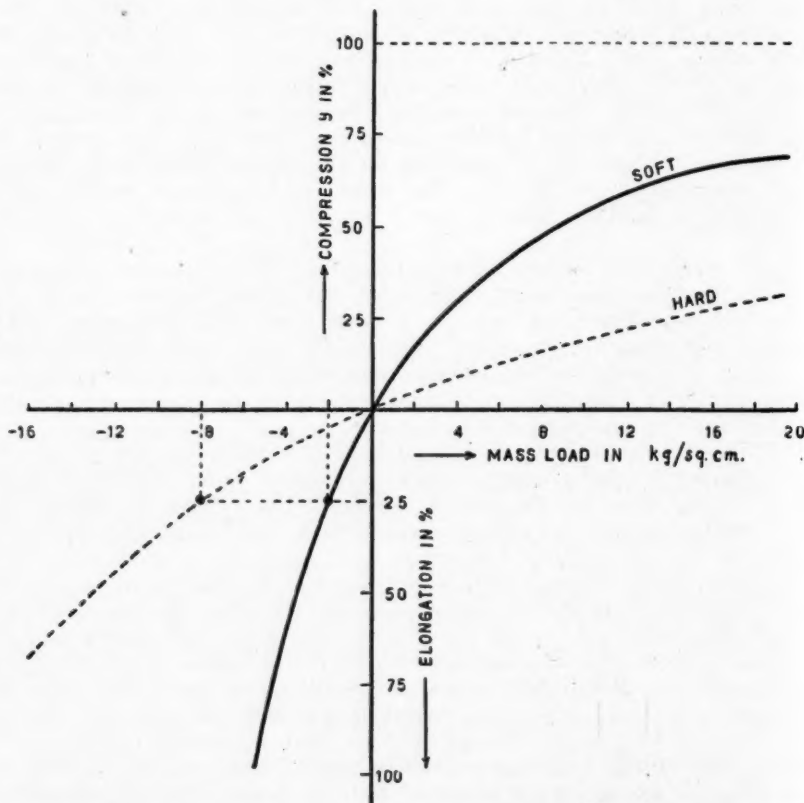


FIG. 1.—Tension and compression curves for a soft and a hard rubber.  $y$  = relative compression.  $x$  = force of compression per sq. cm. of the original surface in kg. per sq. cm.

$x/S$  is drawn in Figure 2. This line is calculated from the hyperbola  $y=f(x/S)$ , and appears to be straight.

It will thus be apparent that with the help of Figure 2, and with  $x$  and  $S$  given, we can read the static compression  $y$ , and can figure out the spring-constant under load. With the computation of the spring-constant, we must consider that rubber, particularly in case of high modulus, conducts itself stiffer dynamically than statically. Figure 3 shows this. Having computed a static spring-constant from Figure 2, we must multiply by  $S_{dyn}/S_{stat}$  to obtain the dynamic spring-constant. This factor can be found at each  $S$  in Figure 3. For

that matter, this correction is not especially important, since the most practical rubber types lie in the field  $S$  equals 2 to 5 kg. per sq. cm. The correction factor is thus not very great, and in computing the resonance frequencies of a system mounted on rubber it is only under the square root.

It was stipulated for these considerations that the rubber be unhindered in its lateral spread. In practice, however, one will make use of the possibility of vulcanizing the rubber to obtain a rigid connection of the different components, both for compression and stretching. The considerations are, however, directly

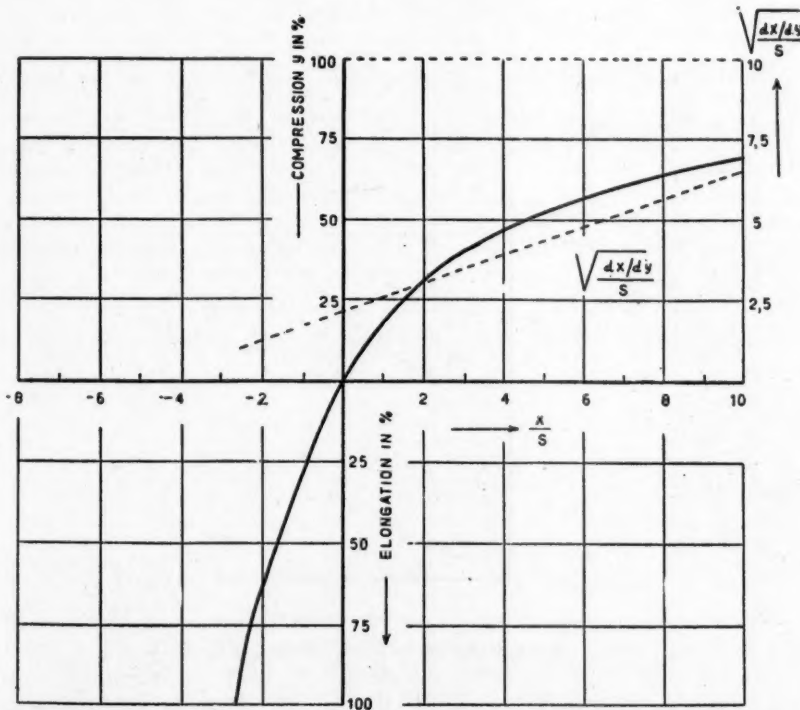


FIG. 2.—Graph whereby the entire elastic conduct of rubber is determined for each type of rubber, valid from 70% compression to  $\pm 100\%$  elongation.  $S$  is the force per sq. cm. of the original surface in kg. per sq. cm. at 25% elongation.

applicable to a cylinder attached through vulcanization, by application of the rule that a strongly vulcanized cylinder with height  $h$  and diameter  $\phi$  must be calculated to have an effective (completely compressible) height equal to  $h_{\text{eff}} = h - \frac{1}{8}\phi$ .

This rule is valid for  $h/\phi > 1/4$ , and amounts to the supposition that with the fixed extremities a layer  $1/16 \phi$  thick is hindered in its lateral spread and therefore, in reckoning the compressibility, must be subtracted from the total height.

Other than graphically, the computations can be done with formulas, which are very simple but not quite so surveyable. The all-including hyperbola has

$$\text{the equation: } \frac{x}{S} y - 1.07 \frac{x}{S} + 5.28y = 0.$$

The coefficient 1.07 in this should really equal one, assuming that the non-linear conduct of rubber is not entirely due to deformation. A slight deviation can thus be traced. From the above equation, the static compression is simply:

$$y = \frac{1.07}{1 + \frac{5.28}{x} S}$$

and the static spring-constant:

$$s = \frac{O_0}{h_0} \frac{dx}{dy} = \frac{O_0}{h_0} \frac{(x/S + 5.28)^2}{5.65} S.$$

Computation of the dynamic spring-constant can be made by the help of Figure 3.

b. Rubber under shear.

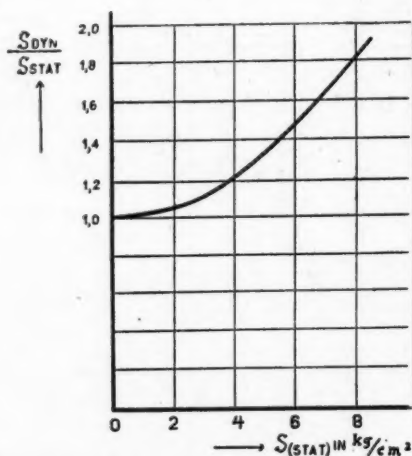


FIG. 3.—Relation between dynamic and static modulus.

Up to now we have been considering the behavior of rubber under compression or stretched. The behavior under shear is much simpler; under shear, the material is not inclined to change in volume, so that deformation does not have to be considered. Since rubber is highly incompressible, the constant of Poisson is:  $m=2$ , through which the gliding modulus  $G$  is calculated simply as  $G = \frac{1}{3} E$ , or figured in our material constant  $S$ ,  $G = 1.65 S$ .

### 3. THE PLANNING OF A RUBBER FOUNDATION

A general scheme for this is difficult, since each case has its peculiarities, which in a general plan cannot be reckoned with. A method of calculation which is useful in many cases is the following:

As data we have the mass and moments of inertia of the machine and the disturbance frequencies. One chooses now categorically between compression- or tension-springs on the one hand, and shear-springs on the other. In general the calculation of the latter will not be difficult. If one chooses compression-



springs, then the next step is that, starting with the lowest disturbance frequency, the position of the resonance frequencies is roughly chosen, f.i. resonances three times lower than the lowest disturbance frequency. The static springing  $f$  is moreover hereby fixed. This is calculated from:  $f = g/\omega_0^2$ , wherein  $g$  is the acceleration of gravitation, and  $\omega_0$  the angle frequency of resonance. This formula is hardly valid for springs with a constant spring-constant; it is, however, accurate enough for preliminary calculations with rubber springs. After the magnitude of  $f$ , one chooses the initial height  $h_0$ , whereby the static compression  $y$  is determined. One must bear in mind here that  $y$  must be smaller than 0.2, or at the most 0.25. This is done on the one hand to avoid plastic deformation; on the other hand it is prescribed for high springs ( $h/\phi=1$ ), since otherwise the spring constant in horizontal direction becomes too small. For compression above  $y=0.3$  to 0.4 a spring of  $h/\phi=1$  becomes unstable. One may call it flexure. From  $y$  follows further  $x/S$  with the aid of Figure 2. When  $h_0$  and  $y$  are known, one chooses  $\phi$ , in connection with the stability in horizontal direction. Usually the ratio  $h_0/\phi_0$  will be  $\frac{1}{2}$  to  $\frac{3}{4}$ . Lower  $h/\phi_0$  ratios give impractically stiff springs, which can be more easily obtained by other methods. Following this,  $S$  is chosen. The rubber types which in our view most merit consideration have a modulus of from 2 to 5 kg. per sq. cm. Higher  $S$  values

TABLE I  
RELATION BETWEEN MODULUS AT 25 PER CENT ELONGATION AND A FEW HARDNESS MEASUREMENTS

$S$ in kg. per sq. cm.	HARDNESS		
	Shore- durometer type A	Schopper ball 10 mm. $\phi$	Pusey and Jones $\frac{1}{4}$ " ball
2	31	150	160
4	44	98	107
6	55	68	74
8	63	53	57
10	68	43	47

will be chosen if one wishes to make a more heavily damping vibration system. Moreover, one then gets a greater difference between  $S_{\text{dyn}}$  and  $S_{\text{stat}}$  ( $=S$ ) (see Figure 3), while generally the plastic phenomena increase with the rigidity. From  $x/S$  and  $S$ ,  $x$  follows, from which further in combination with  $\phi_0$  the mass-load per spring can be calculated, and also the number of springs.

To make the production of rubber of the required modulus easier, we give in the following table the relation between the modulus and a few hardness measurements. Since this relationship does not always strictly hold good, the hardness may be used only for rough orientation. The modulus ultimately remains as the figure that must be watched.

Once more we wish to emphasize that the control of production of such articles must be done by experts. Good results can be obtained only when a strictly adaptable type of rubber is carefully vulcanized by an expert worker.

To avoid these difficulties, most large rubber manufacturers have put vibration dampers on the market. The Continental Werke in Hannover, Germany, for example, supply pressure springs attached to metal plates by vulcanization. The factory requests the machine data, and then furnishes the springs. Another example is shear-springs, produced by Goodrich. The necessary data for these are supplied, so that for each application the desired springs can be chosen. The advantage is that they can be made in almost any desired length, so that in any unforeseen circumstances the support can be slightly altered.

#### 4. ADVANTAGES OF RUBBER COMPARED TO OTHER MATERIALS

As we have already observed, the choice of insulation material is determined through the characteristic advantages and disadvantages of each material; we shall now discuss this briefly.

Summing up, we come to the following conclusions:

##### A. Rubber as against porous material, such as cork, felt, etc.

1. For each type of rubber the material constant  $S$  can be obtained. This can serve as a basis for technical calculations. An article already produced will keep its properties, if not overloaded. Felt and cork lend themselves less readily to technical projects. Moreover, their properties are not unchangeable with time.

2. Rubber has not too much internal friction, as have felt and cork. Also too much damping injures the insulation. If a great deal of damping is necessary, then sponge rubber is the material indicated, since it lends itself readily to calculation and designing, and has as much internal friction as other porous materials.

3. Rubber can be strongly attached to metal through vulcanization. Cork and felt are not attachable.

##### B. Rubber as against spiral springs.

4. Rubber springs have, on the average, a lower specific weight and a higher elasticity modulus than steel springs. Rubber springs are therefore smaller and lighter than corresponding steel springs.

5. In view of the preceding point, rubber springs can be cheaper than steel springs, since the price per kilogram for both materials is about the same.

6. Steel springs are practically frictionless; rubber springs have internal friction. A measurement for the internal friction is the so-called angle of loss, which for steel is  $0.00^\circ$ , for rubber  $\pm 1$ , which increases with the modulus to  $\pm 7$ , for sponge rubber 10–20. This friction is advantageous to the performance of the mounted machine within the range of resonance, while it does not injure the insulation at high frequencies, since the friction decreases in inverse proportion with the frequency. For the contrary see Point 8.

7. Oil dampers next to steel springs, while they give the desired effect at low frequencies, are extremely bad at high frequencies, since the friction constant for high frequencies in itself appreciably increases.

8. Steel springs let through sound-frequencies, as a result of the frequencies of the springs themselves. These are lower in steel, as a result of what was mentioned under point 4, and through lack of much internal friction are much more injurious than in rubber. As experimental proof we point here to an article of Meyer and Keidel *Z. Techn. Phys.* 18, 299 (1937), from which we borrowed Figures 4 and 5.

Figure 4 gives the insulation of a system of solid rubber. Plotted is minus the insulation in decibels against the frequencies in vibrations per second. The negative insulation in the resonance range ( $\pm 100$  Hz) is easy to see, after which a strong increase in insulation can be observed. In Figure 4b the disadvantageous influence of the lowest own-frequency is just visible. Figure 5 shows two curves, taken from spiral springs. The harmful influence of the inherent frequencies, which to a large degree destroys the insulation for acoustic frequencies, is very obvious. With a demonstration this point is made still clearer. A small motor drives a small shaft on which are two eccentrics

with equal eccentricity. On these there hang respectively a steel spring weighing about 1 kilogram and a rubber strip of the same weight. The spring-constant of both is about the same, so that the vertical resonance frequency is the same for both. In the hypercritical zone the rubber scheme remains continually quiet, while the steel shows a few resonances. One resonance at  $\pm 3000$  r.p.m. is very strong, and imposes a vibration of the magnitude of 1 mm. on the weight. The mass-forces required appear on calculation to be of the order of magnitude of 10 kilograms.

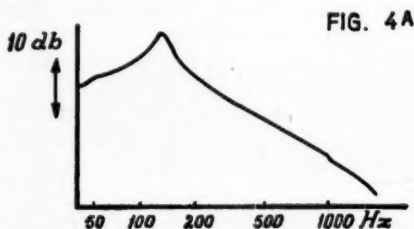


FIG. 4A

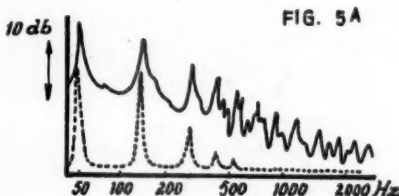


FIG. 5A

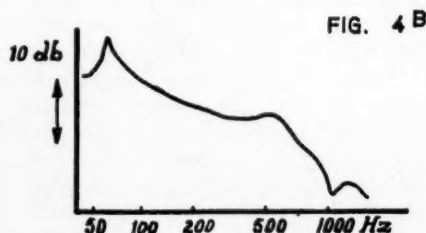


FIG. 4B

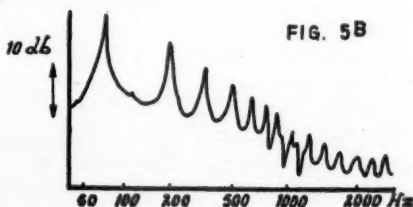


FIG. 5B

FIG. 4.—Insulation through rubber. Practically no disadvantageous influence through self-frequencies. Compare Figure 5.

FIG. 5.—Insulation through spiral springs. The insulation is greatly injured by the self-frequencies of the springs.

### 5. A FEW SPECIAL CASES OF INSULATION

We shall conclude by mentioning a few insulation cases, wherein rubber can prove serviceable.

Rubber is excellent when used as a shock-absorber or buffer. In this use the bent compression curve of rubber is very satisfactory, since hereby the buffer is supple for slight bumps and proportionally stiffer for heavier ones.

Further we mention elastic couplings, whereby accurate centering is superfluous and insulation appears, and water-lubricated rubber cushion blocks, which, aside from being capable of insulation, have the advantage of not being subject to wear.

Without going into this further, we shall in conclusion point out the excellence of rubber under tension load. It is easy to calculate that a rubber spring at 100% elongation, as far as the spring-constant is concerned, is equivalent to a spiral spring which carries the same load with twice as great an elongation.

# A QUANTITATIVE METHOD OF EXPRESSING FLEX-CRACKING RESULTS \*

R. G. NEWTON

The degree of flex-cracking produced by flexing machines such as the De Mattia or the Du Pont machines is normally a difficult quantity to evaluate with any precision, owing to the arbitrary surface cracking that must be assessed before any measure can be made of the amount of breakdown which has occurred. For this purpose, two systems are in general use. The first employs the number of flexing cycles required either to break the specimen or to produce the first appearance of cracking<sup>1</sup> and the second method uses some type of comparison chart, consisting usually of specimens which have been flexed to different stages in the breakdown process, or photographs of those specimens. The first method usually gives the more variable results and is not to be recommended.

When the comparison chart method is used, the specimens or photographs have hitherto been numbered with equally spaced numbers. For example, the standard method of the American Society for Testing Materials (D 430-35 T) recommends the numbers 0 to 10, and this scheme is followed by Somerville<sup>2</sup> and the Vanderbilt Company<sup>3</sup>, while Neal and Northam<sup>4</sup>, using the Du Pont grooved-belt method, number their scale from 0 to 8. This procedure gives the impression that equal increments of flexing breakdown are represented in passing from one number on the chart to the next, although no evidence is provided that this is, in fact, the case. The American Society for Testing Materials (*loc. cit.*) state: "The standard comparison scale shall consist of ten specimens equally graded and numbered from No. 0, showing no cracking, to No. 10, which is completely cracked through", but there seems to be no reliable means of ensuring that the grading shall be equal. It is the qualitative nature of this scaling, as well as the lack of reproducibility of the test results and the uncertain equivalence with service tests, which is responsible for the criticism of the method as a specification test. Before these objections can be overcome, it is necessary to have available a quantitative scale for expressing the extent of flex-cracking resistance of the sample.

A novel method of determining the degree of breakdown is that advanced by Rainier and Gerke<sup>5</sup>, in which the decrease in bending moment is used as the measure. These authors also point out the urgent need for a reproducible precision test, and desire to achieve this object by initiating the cracking with ozone, which is done in two stages. The subsequent flexing process is carefully controlled, and the extent of the flexing breakdown is determined by measuring the force required to bend the specimen through an angle of 45 degrees, as the surface cracking produced by the flexing leads to a reduction in the resistance to bending. This method, although interesting, may require several weeks to give the final result; it needs some skill in handling and does not appear to be more accurate than the simple method proposed in this paper. Rainier and Gerke<sup>5</sup> assert that the slow rate of breakdown, with the consequent lengthy experiment, is essential for duplicating road service conditions and that "it is believed that what is lost in time may be gained in validity". The author is not in a position to assess the economics of this statement.

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 15, No. 3, pages 172-184, October 1939.

Since in the application of a particular comparison chart, the numbering of the successive stages of cracking in arithmetic progression must, in general, be unjustifiable, the photographs of cracked specimens used in a new chart in the laboratories of the Research Association of British Rubber Manufacturers were designated qualitatively by letters A, B, C, D, E, F, G, H, J, K, in order of increasing breakdown (Figure 1).

The first problem discussed in the present paper is that of evaluating these symbols in numerical terms, that is, of determining the quantitative relations existing among the various degrees of breakdown.

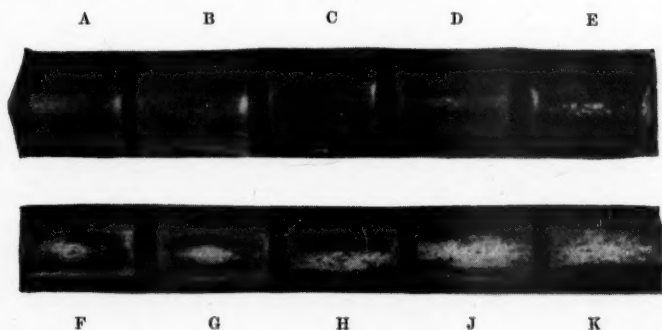


FIG. 1.

#### THE PRINCIPLE OF THE SCORING SYSTEM

Fortunately, there has recently been invented (1935) a statistical method which provides a ready solution of this problem, with, moreover, surprising accuracy. This method is that of discriminant function analysis, which was devised by Fisher, originally for the purpose of evaluating the results of scoring systems employed in anthropometric studies involving skull measurements<sup>6</sup>. Since this first application, the method has attained success in solving a bewildering variety of biological scoring problems. It has been employed by Fisher<sup>7</sup> for studies in plant taxonomy, describing in metrical terms the differences between nearly related plants, and determining what combination of flower characteristics provides the greatest discrimination between three species. In a similar manner Smith<sup>8</sup> has provided a precise measure of the economic value of wheat varieties, so that the results can be assessed of wheat-breeding experiments designed to improve flour quality. The method has also been used by Wallace and Travers<sup>9</sup> to measure the qualities of a specialty salesman, and by Day<sup>10</sup>, who has determined the haulage costs of logs of different diameters from a knowledge of the composition of different loads having the same haulage cost. Much progress, as yet unpublished, has been made in the evaluation of certain blood sera reactions<sup>11</sup> and recently Fisher<sup>12</sup> has reviewed the position.

It was accordingly realized that this method of analysis would probably be of value in placing the crack-scoring on a quantitative basis, and the necessary mathematical computations have been kindly and ably made by W. L. Stevens, of the Galton Laboratory, University of London. It is hoped that the details will be published in full elsewhere, so that only a brief description of the process will be included here.



The principle underlying the derivation of the quantitative scoring can be illustrated as follows, and an explanation, in more mathematical terms, will be given later. Each letter represents a certain amount of breakdown, the numerical value of which is unknown. The differences between these amounts of breakdown could be expressed in terms of the number of flexing cycles<sup>13</sup> which are required to bring about the increase of breakdown implied in passing from one letter to the next. In determining this number of cycles per step, two difficulties are at once evident. In a test of one sample, readings cannot usually be taken at (say) grade B exactly: the scoring, B, means merely nearer to B than to A or C, and consequently the number of flexing cycles between letters is difficult to determine. Secondly, even if a value could be obtained for one vulcanizate, it might not be the same for another vulcanizate.

Both of these difficulties can, however, be overcome, and the method for so doing can be illustrated by the following hypothetical considerations. Suppose a large number of test results from different vulcanizates are available, and suppose that numbers representing the scoring constants were allotted to the letters by bad guess-work; then values of the flexing resistance of each sample could be calculated, but the values would be wrong. Call these incorrect values the calculated values. If the true values of the flexing resistance were known, the error, or difference between the true and calculated values, could be evaluated.

If better guess-work had been used, the error would be less than in the first case. In fact, the smallness of the error would be a measure of the success of the guessing process, and the scoring constants would have their best possible values when the error had its minimum value. There must always be some error, as the minimum amount represents the experimental error, including that due to the discontinuities of the scale. Discriminant function analysis provides a means of calculating the scoring constants so that the error shall be a minimum, or, in other words, numerical values (scoring constants) are given to the qualitative letters in such a manner as to reduce to a minimum that portion of the total variation among the quantitative results (for each rubber) which is not accounted for by the scoring. Naturally, the greater the number of results which are included in this process, the more accurate and representative are the final values of the scoring constants.

In actual practice a large number of tests would be made on vulcanizates of a range of types which would comprehensively cover future applications of the test method. In the present instance the results from only twenty samples were used, and although the range of rubbers was somewhat restricted, the conclusions suffice to demonstrate the value of the new method. As various disadvantages of the test procedure have appeared as the result of this analysis, a detailed description of the rubbers will not be included, and the paper must be regarded mainly as an account of this new principle by which the results may be scored.

#### DERIVATION OF THE SCORES

The qualitative results obtained are given in Table I, and it is evident that the actual point of breakdown is very uncertain, one specimen breaking at G and others going to K, where they appear to stay almost indefinitely. For this reason the actual breaking of the specimen must be regarded as a rather arbitrary phenomenon, and it is easy to see why flexing results which are determined from the breaking of the specimen are more variable than those in

which some intermediate point of breakdown is employed. In this respect, the process is analogous to tensile testing of rings with the Schopper machine, where the error in measuring the load at break is greater than that in determining the load at a lower elongation.

Since, moreover, the final stages of breakdown are of no practical interest to the rubber manufacturer, who is sufficiently concerned if only cracks appear;

TABLE I.  
QUALITATIVE DATA FOR TWO DUPLICATE SERIES OF FLEXING TESTS ON TEN VULCANIZATES, THE TWO SERIES BEING PERFORMED AT DIFFERENT TIMES.

First series of tests.										Total number of flexing cycles.	Second series of tests.									
Vulcanizates.											Vulcanizates.									
1	2	3	4	5	6	7	8	9	10		1	2	3	4	5	6	7	8	9	10
			A	A			B			4,500							B			
		A	A	A			C			9,000							B			
		A	D	C			C			13,500							C			
		A	E	E		B	C			22,500				B		A	C			
		C	F	C			C			31,500	A	A	B	C	F	A	C	D		
		C	H	G			D			40,500	A	A	C	D	K	B	E	D		
		D	H	H			F			49,500	B	B	C	E	K	B	F	D		
		D	H	H		A	E			58,500	C	C	D	H	K	D	G	D	A	
		E	J	J			G			67,500	C	D	E	J	K	E	G	D	B	
							D			85,500	C	D	E	K	K	F	G	D	C	
A	B							A	B											
C	C	F	K	K	D	H	G	B	B	103,500	C	E	F	K	K	F	H	D	G	
C	D	G	K	K	E	H	G	B	B	121,500	C	F	H	K	K	H	H	E	G	
C	D	G	K	K	F	H	G	B	B	139,500	D	G	J	K	K	J	H	H		
C	D	G	K	K	G	J	J	D	C	157,500	E	H	K	K	K	J	H	H	G	
D	D	H	K	K	G	J	J	E	H	175,500	E	H	K	K	K	J	H	H		
D	E	H	K	K	G	J	J	F	H	193,500	F	J	K	K	K	K	H	J	H	
E	F	H	K	K	H	J	J	G	H	211,500	G	K	K	K	K	K	J	J	J	
E	F	H	K	K	H	K	J	G	H	229,500	G	K	K	K	K	K	J	J	J	
E	F	H	K	K	H	K	J	G	H	247,500	G	K	K	K	K	K	J	J	J	
F	G	H	K	K						265,500	G	K	K	K	K	K				
F	G	H	K	K	J			H		283,500	G	K	K	K	K	K	K		J	
G	G	H	K	K	J			H		306,000	G	K	K	K	K	K	K		J	
G	G	H	K	K	J			H		324,000	H	K	K	K	K	K	K		J	
G	G	H	K	K	K			H		360,000	J	K	K	K	K	K	K		J	
G	G	H	K	K	K			H		400,000	J	K	K	K	K	K	K		J	

A thick horizontal line denotes complete rupture of the test-piece.

it was decided to use only the first five stages (A to E) for the discriminant function analysis; this procedure has an additional advantage in reducing the mathematical labor involved. Another consideration involving rejection of the readings corresponding to the more severely cracked stages exists in the different stretch to which the surface is subjected. After much cracking has occurred, the average surface strain is less, and the breakdown will proceed more slowly, as is shown by the great number of letters of the same kind which are found when stage F is passed (see Table I, particularly vulcanizates 4 and 5).

If, as a preliminary measure, the qualitative (letter) scorings are allotted the equal intervals for which they were intended, and for each vulcanizate, the values are plotted against the number of flexings, lines are obtained which suggest that the rate of breakdown at a given time is inversely proportional to that time. Thus, those rubbers in which the first cracks appear only after many flexings also break down very slowly in the subsequent stages. This result suggests that the number of flexings should be expressed on a logarithmic scale so that the apparent (logarithmic) rate of breakdown would be independent of the time taken to reach a given state of breakdown. All the lines representing the progress of breakdown will then be roughly straight, will be parallel to one another, will all have the same slope, and will differ only in their positions along the logarithmic axis: the positions can then be used as a measure of the flexing resistance.

This logarithmic interpretation, besides having statistical advantages in reducing the number of parameters to be estimated, has a rational basis, as the resistance to flexing breakdown can be expressed in two ways:

- (1) as the time taken to show the first signs of breakdown;
- (2) as the rate at which breakdown proceeds after it shows signs of having started.

TABLE II

Qualitative score	Quantitative scoring constants
A	+ 0.327
B	+ 0.146
C	0.000
D	- 0.155
E	- 0.282

An inverse equivalence of these two methods of expression would imply this logarithmic relationship, except that the relationship would break down when the flexing resistance was very poor (see below).

Hence, at least as a tentative hypothesis, the scoring constants should be arranged to provide the minimum deviation from a set of regression lines which have a common slope, but different positions, for different vulcanizates. It is this condition which ensures that the error, as described above, is made as small as possible.

In a preliminary analysis, it was found that rubber No. 8, with a very small flexing resistance, broke down in a manner quite different from that of all the others and, consequently, for the purposes of this preliminary investigation, rubber No. 8 was discarded from the analysis.

The labor of calculating the scoring constants, which is illustrated in papers by Fisher<sup>7</sup>, Smith<sup>8</sup>, and Wallace and Travers<sup>9</sup>, and which, in the present case, will be published by W. L. Stevens, need only be carried out once, the subsequent use of the values being very simple. In this instance it was found that the spacing between the values was not equal, although the variation from equality was not large. The actual values are given in Table II, the value of C having been made equal to zero, as it is in the middle of the range, A to E, and represents a convenient level of breakdown for use as a reference.

When the grading is A or B, the state of the samples is better than that at grade C, and this is indicated by the positive sign of the scoring constant. Each

qualitative scoring observed can now be used to give an estimate of the number of flexing cycles equivalent to state C, merely by adding the scoring constant to the logarithm of the number of flexing cycles, as is illustrated in Table III which represents the calculations for rubber No. 7 in test 1.

TABLE III

Original data		Derived data		Result
Actual number of flexing cycles when reading was taken	Qualitative score registered	Logarithm of No. of flexings 1,000	Quantitative scoring constant corresponding to the letters	Estimate of flexings log. (1,000) required to reach level C. = score
22,500	B	1.352	+ 0.146	1.498
31,500	C	1.498	+ 0.000	1.498
40,500	D	1.607	- 0.155	1.452
49,500	E	1.695	- 0.282	1.413

Mean 1.46  $\equiv$  29,170 flexing cycles.

It is thus evident that a reliable estimate is provided of the logarithm of the number of flexings required to produce condition C (the score for the rubber). The actual number of flexings required is 29,170, but it is probably more convenient, and certainly more rational, to retain the score 1.46 to express the degree of flex-cracking resistance of rubber No. 7 under the conditions of test 1.

#### CONFIRMATION OF LOGARITHMIC HYPOTHESIS

It is now possible to test the validity of the use of logarithms of the numbers of flexing cycles. By using the scoring constants, the actual regressions of scoring constants on the logarithm of the flexings can be calculated. In deriving the scoring system, the common slope to all the lines was arranged to have a regression coefficient equal to  $-1.0$ . If the logarithmic hypothesis does not represent the actual conditions, any discrepancy can most readily be detected by comparing rubbers which have very good and very bad flex-cracking resistances, *e. g.*, vulcanizates 1, 2, 3, and 5. Table IV gives the score for the

TABLE IV

#### TEST OF THE LOGARITHMIC HYPOTHESIS

Vulcanizate No.	Flex-cracking resistance		Regression coefficient (scoring constant on log. flexings)
	Score	Number of flexings to produce grade C	
1	2.1027	126,700	- 1.003
2	2.0154	103,600	- 0.914
3	1.5896	38,870	- 0.909
5	1.3265	21,200	- 1.156
Mean			- 0.996

rubber (with the conversion into the actual number of flexing cycles to produce state C), and the regression coefficient calculated from the scoring constants. If the logarithmic scaling of the flexings is valid, this last quantity should have the value  $-1.00$ .

Not only are the differences from  $-1.0$  in each case small, but, more important, there is no definite trend in the values, which would occur if the hypothesis

had broken down and the more resistant rubbers had followed a course different from the less resistant ones. The hypothesis must break down when the number of flexings approaches zero ( $\log. 0 = -\infty$ ), but it is evident that: (1) if appreciable flex-cracking occurs after only a few cycles, there is no point in evaluating the flex-cracking resistance, and (2) the hypothesis holds well for the weakest rubbers used, with the exception of No. 8, which showed the first cracks after about 1,000 cycles. There is, therefore, no reason to distrust the assumption that, on a logarithmic scale of flexings, vulcanizates differ only in respect to the score and not in apparent rate of breakdown. The scores can thus confidently be taken as the measure of flex-cracking resistance of the rubber.

It is interesting to note that the use of logarithms in this manner assists the interpretation of the results obtained by Rainier and Gerke<sup>6</sup>. These authors say " . . . the rate of growth of cracks . . . is constant up to about 60 per cent loss of bending moment", and their Figure 6 shows straight lines drawn through the points lying between 10 per cent and 60 per cent deterioration, whereas above 60 per cent the line becomes markedly curved. However, if logarithms of the numbers of flexing cycles are employed, a straight line can be drawn through the points lying between 20 per cent and 90 per cent deterioration, and the fit actually appears as good as that for Rainier and Gerke's line. Thus, in the case of their sample 2, illustrated in Figure 6, using the points between 10 per cent and 60 per cent deterioration, the mean square accounted for by the regression is 2,230, while the residual variation has a mean square of 2.00 giving a variance ratio of 1,115. When logarithms of the numbers of flexing cycles are employed, the mean squares are 4,737 and 4.94, respectively, while the variance ratio is 962.

#### ACCURACY

The consistency in calculating the scores has been indicated in the case of rubber No. 7, but it will be more interesting to consider the error present in the entire data. This can best be determined by an analysis of variance carried out using all the scores. If this is done, the accuracy appears surprisingly great, as of 99 degrees of freedom, 82 for error represent only 11 per cent of the total variance, and it is possible to show that there is a very significant difference between tests 1 and 2, which were intended to be exact replicates. Actually, the standard deviation of the difference between the two repeat tests is 0.856 (on the basis of a single observation), whereas that for the error is only 0.095. The value of the variance ratio is 80.4, but the tabled value for a probability of one in a thousand is about 11.5. It is clear that the precision of estimation has far outrun the present accuracy of repeating the tests, that is to say, the preparation and testing of samples from the same mixing, the conditions of the second test being as far as possible identical with those of the first. This lack of reproducibility has been found by many other workers, but it has not before been possible to measure the discrepancy with such convenience.

For the experiment reported above, the standard deviation of a single observation is a constant amount, independent of the flex-cracking resistance, and equal to 0.095, and the value of the scores representing the breakdown resistance might vary between (say) 0.5 and 3.0. In this test the average number of observations made on a sample appears to be about six (within the range A to E; see Table I), so that the standard error of a mean score, *i. e.*, final result of test, would be about  $\pm 0.04$ .



Since performing the experiments reported above, the accuracy has been improved considerably, due to consideration of the following points. It is possible to calculate the minimum value for the residual variation, *i. e.*, that unaccounted for by the regression and due simply to the discontinuities of the qualitative scale. The standard error of the actual residual variation is found to be only twice this theoretical minimum value. This suggests that the accuracy of measurement is to some extent limited by the coarseness of the scale, and that half-way scores would be desirable; in fact, the test operator had remarked that there were occasions on which he was in some doubt whether to grade by the upper or lower letter. An actual example will make the question clear. Table V gives the calculations for rubber No. 3 in test 1, the results obtained being given in the first five columns. It is clear from the values of the scores that the first one is unduly low and consequently the condition of the cracks was really better than A, so that it should perhaps have been recorded as grade A+, the positive sign indicating the superior condition. Similarly, the second score is unduly high, and the true grading might have been A-, with a

TABLE V  
CALCULATIONS FOR RUBBER NO. 3 IN TEST 1

Number of flexing cycles	Log. flexings ( $\frac{\text{flexings}}{1,000}$ )	Scoring constant		Score	Alternative grading and constant		New score
13,500	1.130	A	+ 0.327	1.46	A +	+ 0.417	1.55
22,500	1.352	A	+ 0.327	1.68	A -	+ 0.237	1.59
31,500	1.498	C	0.000	1.50	C +	+ 0.073	1.57
40,500	1.607	C	0.000	1.61	C	0.000	1.61
49,500	1.695	D	- 0.155	1.54	D +	- 0.078	1.61
58,500	1.767	D	- 0.155	1.61	D	- 0.155	1.61
67,500	1.829	D	- 0.155	1.67	D -	- 0.218	1.61
85,500	1.932	E	- 0.282	1.65	E	- 0.282	1.65
				Mean 1.59			
					Mean 1.60		

value of the scoring constant half-way between those for A and B. The scoring constant for A+ can probably be taken above A at a distance equal to half the interval A to B. In the same way, maintaining the letters of the original grading and merely adding signs where they appear appropriate, an alternative grading can be devised as indicated in column six, from which is derived the new score in column eight. These new scores appear far more consistent, and the standard deviation is only 0.031, compared with 0.083 for the original scores. This marked improvement in accuracy suggests that originally the states of breakdown were scored only as accurately as was possible without employing these half-grades.

It may be noted that the values of the new scores appear to increase as the breakdown proceeds, suggesting that the scoring constants are not graded suitably. Subsequent experience has shown that these very early crackings at A+ are really about a full grade above A, which would raise the first value of the new scores to about 1.67 and destroy this illusory increase.

Another question of great importance in ensuring accurate grading is that of the intervals of the scale of numbers of flexings. The scale of flexing cycles in Table I was arranged to provide for gradually increasing intervals of flexing cycles; the two extreme ends of this scale are reproduced in Table VI, together with the appropriate logarithms and the intervals on the logarithmic scale.

As the average difference between the successive scoring constants is about 0.15, it is clear that the intervals of the scale of log. flexings are much too large at the beginning and unnecessarily close at the end. The first interval is even greater than that corresponding to a difference between two grades, and must lead to great inaccuracies in the scoring of poorly resistant samples. It is evident that the numbers of flexing cycles corresponding to the observation points should be chosen to provide a scale of equal increments on the logarithmic basis and, moreover, the logarithmic interval should be arranged to accommodate grading by half-steps, *i. e.*, the logarithmic interval should be 0.07; or the flexing numbers in the ratio 1.00:1.17. This latter provision will also have the advantage of doubling the number of observations made on each sample and, consequently, of further reducing the standard error of the mean score.

Experiments arranged on such a basis have given a standard deviation of

TABLE VI

Scale of numbers of flexing cycles	Scale of log. ( $\frac{\text{flexings}}{1,000}$ )	Intervals on the log. scale
4,500	0.653	
9,000	0.954	0.301
13,500	1.130	0.176
22,500	1.352	0.222
31,500	1.498	0.146
283,500	2.453	
306,000	2.486	0.033
324,000	2.510	0.024
360,000	2.556	0.046
400,000	2.602	0.046

0.050 (on 79 degrees of freedom) instead of 0.095, as above, and as the average number of observations is now 11, the standard error of a mean score (final result) is  $\pm 0.015$ . The flex-cracking resistance of a single test specimen of a medium-resistance rubber can therefore be expressed as (say)  $1.50 \pm 0.03$ , the  $\pm$  limits indicating the values outside which the true mean is unlikely to fall. The constant standard error represents about a 3.5 per cent difference in the number of flexing cycles, and a comparison could thus be made with other methods of determining the flex-cracking resistance in which the number of flexing cycles is employed.

The only other method which supplies quantitative results is that proposed by Rainier and Gerke<sup>6</sup>, but they do not give figures for their error of measurement. Calculations based upon their Figure 6, however, suggest that the slope of their line, which they employ as the measure, has a standard error of about 3.8 per cent. The only figures which they give are probable errors which apply to the variation between test-specimens of one type of rubber, and it is clear that some mistake has been made in their statistical calculations, since either the probable errors or the levels of significance are wrong. If, as appears likely,

the mistake is in the levels of significance, the standard error of a mean obtained from six specimens would be about 6.5 per cent of the number of flexing cycles.

The investigation described in this paper does not supply a satisfactory estimate of the variation among samples of one rubber, but other work carried out at the Research Association of British Rubber Manufacturers suggests that 9.5 per cent would be a comparable figure based on the number of flexings, obtained with the method proposed in this paper. This comparison has, however, no bearing on the accuracy of the test method and it merely suggests that Rainier and Gerke<sup>5</sup> can reproduce their samples more accurately, or alternatively, that their initiation of cracking by means of ozone does decrease the great variation between specimens which are intended to be identical.

### CONCLUSIONS

In addition to providing a means of obtaining accurate quantitative results for individual flex-cracking tests, such as the De Mattia or Du Pont tests, the application of discriminant function analysis suggests a basis for standardizing the entire test method, so that objection to the test for specification purposes is thus concerned only with the reproducibility of the results, a problem which can now be investigated with greater confidence and ease.

In connection with the accuracy of the method it may be contended that much depends on the subjective attitude of the tester who grades the samples with the photographs. When half-scores were not employed, the accuracy was limited mainly by the coarseness of the scale. This suggests that the grading is objective and, although no comparison, based upon statistical methods, has been made to determine the discrepancies between operators, no circumstance has occurred to suggest that important divergencies of opinion do exist. In addition, the analysis has been repeated on a further series of fifty samples, and the values found for the scoring constants were not substantially different from those obtained in this investigation.

There is thus good reason to believe that this method of assessing the results will form a valuable means of investigating the causes of variation in flex-cracking test results and of recording the conclusions from the tests.

The author wishes to thank the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish the results given in this paper.

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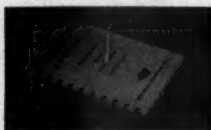
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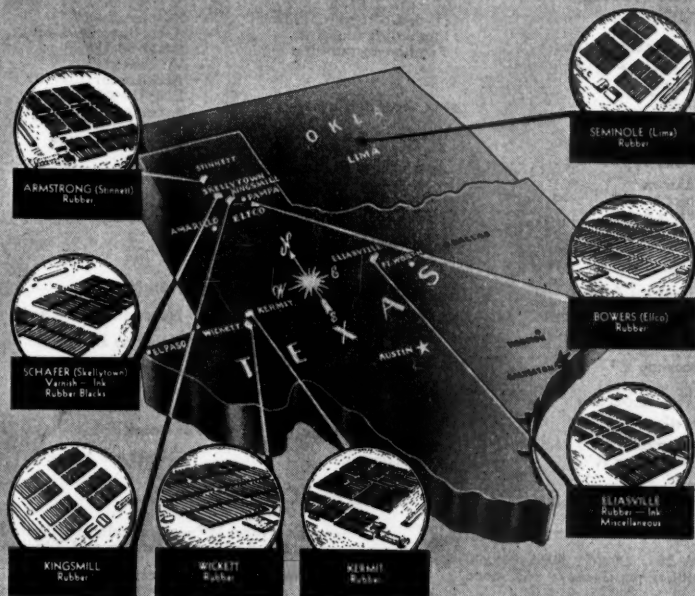


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